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A DETERMINATION OF THE MAGNETIC SATURATION INDUCTION OF IRON AT ROOM TEMPERATURE

By Raymond L. Sanford and Evert G. Bennett

ABSTRACT

A determination of the magnetic saturation induction of iron at room temperature has been made, using a modification of the Ewing isthmus method. Specimens were taken from several ingots of iron of exceptional purity prepared at the National Bureau of Standards. Corrections were made for the effect of the small amounts of impurities present, and care was taken to minimize systematic and accidental errors. The value found for pure iron at 25° C, assuming a density of 7.874 g/cm^3, is 21.58 ±0.01 kilogauss.

CONTENTS

		Page.
I.	Introduction	1
II.	Previous determinations	2
III.	Method and apparatus	2
IV.	Calibration and adjustment	4
V.	Test specimens	7
VI.	Final observations and results	9
VII.	References	12

I. INTRODUCTION

The determination of the magnetic-saturation value of iron at room temperature reported in the present paper was undertaken as part of a more extensive program initiated some time ago by the Division of Metallurgy of the National Bureau of Standards for the purpose of investigating the fundamental properties of pure iron. To this end, Thompson and Cleaves [1] [1] prepared several ingots of exceptionally pure iron. This material compares favorably with any previously produced, not only with respect to purity but also with respect to the accuracy to which the amounts of the impurities have been determined. The preparation and analysis of the material are fully described in the paper cited above. The total amount of impurities out of 55 elements sought was of the order of 0.01 percent, of which carbon did not exceed 0.001 percent.

Ten of the ingots were selected as being representative of the maximum range of impurities, both with respect to the total amount and with respect to individual impurities, and magnetic test specimens were prepared from these ingots. Data on the compositions of the individual ingots are given in table 1.

[1] Numbers in brackets indicate the references at the end of the paper.

TABLE 1.—*Composition of ingots*

Ingot number	Impurities								
	Be	C	Cu	H_2	N_2	O_2	S	Si	Total[1]
	%	%	%	%	%	%	%	%	%
3	<0.001	0.001	<0.002	0.000_1	0.000_4	0.000_8	0.002_6	0.003	$<0.011_1$
6	<.001	<.001	<.002	$.000_3$	$.000_2$	$.004_5$	$.001_3$	.001	$<.011_7$
7	nil	<.001	<.002	$.000_3$	$.000_1$	$.002_0$	$.002_1$	.001	$<.008_8$
8	nil		<.002	$.000_2$	$.000_0$	$.003_2$	$.001_8$	.001	$<.008_8$
12	nil	<.001	<.002	$.000_2$	$.000_5$	$.001_4$	$.001_3$	.002	$<.008_4$
13	nil	<.001	<.002	$.000_1$	$.000_3$	$.004_0$	$.002_4$	nil	$<.010_3$
14	nil	.001	<.002	$.000_1$	$.000_2$	$.002_0$	$.001_1$	0.002	$<.008_9$
18	nil	.001	<.002	$.000_2$	$.000_1$	$.000_4$	$.001_1$	nil	$<.008_2$

[1] Including allowances for elements not determined in the individual ingots, based on average amounts found in other ingots.

II. PREVIOUS DETERMINATIONS

The first magnetic measurements with very strong fields were made in 1889 by Ewing and Low [2], who reported a saturation induction of 21.36 kilogausses for a sample of wrought iron of unspecified purity. They used their now well-known isthmus method. Since that time several values have been reported, ranging from 21.26 to 22.58 kilogausses. This range of about 6 percent may be attributed partly to inaccuracies in measurement and partly to the effect of impurities in the materials. Apparatus and experimental technique have been improved, and the effects of various common impurities have been determined, so that recent values are in much better agreement.

In 1918 Gumlich [3] reported a value of 21.62 kilogausses, which for several years was the most generally accepted figure. He used a "yoke-isthmus" method and corrected for the effect of certain impurities. Three later investigations carried out in different countries and by different experimental methods yielded results differing very little from that given by Gumlich. In 1926 Honda and Kaya [4] in Japan, working with single crystals of iron, obtained a value of 21.58 kilogausses. In 1929 Weiss and Forrer [5] in France, using small ellipsoids magnetized between the poles of an electromagnet, obtained a value of 21.56 kilogausses, assuming a density of 7.878 g/cm^3. The latest report comes from the Physikalisch-Technische Reichsanstalt, in Germany, where, in 1937, Steinhaus, Kussmann, and Schoen [6] obtained 21.58 $\pm$0.01 kilogausses. They used a somewhat modified form of Gumlich's yoke-isthmus method and corrected for the effect of impurities. Their value also is based on a density for pure iron of 7.878 g/cm^3.

III. METHOD AND APPARATUS

In the present investigation, a method based upon the isthmus method of Ewing and Low [2] was adopted, because by this method magnetizing forces up to 10,000 oersteds can be applied with a moderate expenditure of power and without undue heating of the specimen. Furthermore, the space within which the magnetizing field is measured is easily accessible, so that its uniformity can readily be investigated.

The apparatus employed was the High-H permeameter [7] with special pole pieces and test coils. The arrangement of the pole pieces

and test coils is shown in figure 1. Extension pieces, E, on which are screwed the pole pieces, *P*, are inserted in the poles, *C*, of the permeameter. The pole pieces and extensions are drilled axially to permit the insertion of the specimen, *S*.

The magnetic circuit is completed by two large laminated U-shaped yokes (not shown) The main magnetizing coils, *M*, surround the poles, but there are some additional windings on the yokes.

The test-coil system, *T*, consists of five concentric and coaxial coils of 200 turns each of No. 44 AWG enamel-covered copper wire

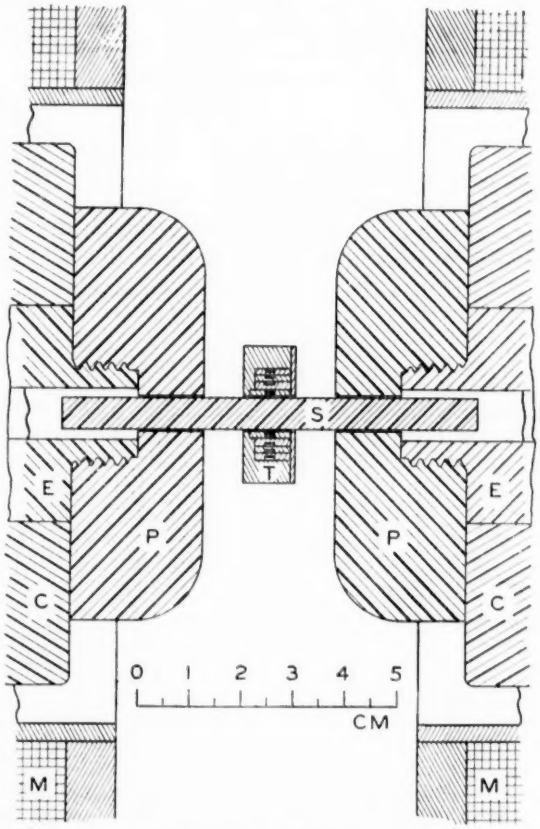

FIGURE 1.—*Arrangement of pole pieces and test coils.*

wound on hard-rubber forms. The coils are 2 mm long. Their effective diameters, as determined from values of area-turns, are 7.22, 7.84, 10.86, 13.52 and 15.78 mm, respectively. These diameters correspond to distances of 0.61, 0.92, 2.43, 3.76 and 4.89 mm, respectively, from the surface of a specimen 6 mm in diameter. By means of a selector switch, it is possible to connect these coils to a ballistic galvanometer in any one of several combinations.

The ballistic galvanometer has a natural period of approximately 30 seconds. The external resistance for critical damping is about

40,000 ohms. However, since the external resistance is generally less than 200 ohms, the galvanometer performance closely approximates that of a fluxmeter. The sensitivity is adjusted in the usual way, using a mutual inductor, standard resistor, and potentiometer. The precision with which the galvanometer deflections can be read is greatly improved by lenses mounted in front of the galvanometer scale.

IV. CALIBRATION AND ADJUSTMENT

The accuracy usually claimed for the results obtained in the determination of the magnetic saturation value of iron is of the order of 0.05 percent. In view of the fact that an accuracy of 1 percent is considered to be very good for ordinary measurements of the magnetic properties of materials, it is obvious that in order to achieve an accuracy of 0.05 percent, it is necessary to take unusual precautions and to consider some sources of error which generally can be ignored. This is particularly true with respect to systematic errors, which can not be minimized by averaging the results of several observations.

The final accuracy of any measurement involving the deflections of a ballistic galvanometer depends directly upon the accuracy to which

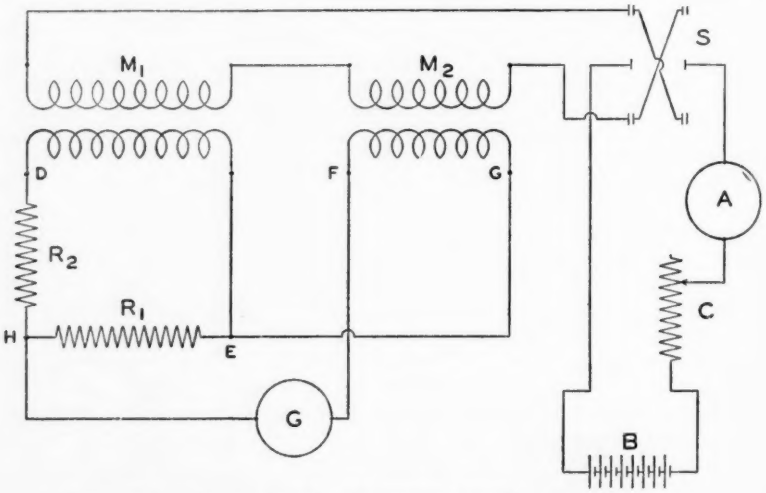

FIGURE 2.—*Connections for the comparison of mutual inductors.*

the value of the mutual inductor used for calibration is known. It is difficult by the usual methods of measuring mutual inductance to obtain an accuracy much better than 0.1 percent. This obviously would be inadequate for the present purpose. Fortunately, there was available a mutual inductor constructed by the Resistance Measurements Section of this Bureau for use in connection with the determination of electrical resistance in absolute measure. Its value is known to 20 parts in a million, or 0.002 percent. The mutual inductors used for the calibration of the ballistic galvanometer were measured by comparison with this standard by the method indicated in figure 2. M_1 and M_2 are the mutual inductors to be compared, of which M_1 must have the greater value. The primary coils are connected in series to

the battery through a reversing switch, rheostat, and ammeter. The secondary coils are connected in opposition, as shown. R_1 and R_2 are calibrated precision rheostats and are adjusted to such values that there is no residual deflection of the galvanometer upon reversal of the primary current. When balance is obtained, the value of M_2, in terms of M_1, is

$$M_2 = M_1 \frac{R_1}{R_1 + R_2}.$$

The resistance of M_1 and its connections must be included in the value of R_2. The usual precautions against the effect of stray fields were taken by separating the two inductors by some distance and so orienting them as to avoid interaction between the primary of one inductor and the secondary of the other.

The accuracy attainable by this method depends upon the magnitude of the inductances, their ratio, the accuracy to which the resistances R_1 and R_2 are known, and the sensitivity of the galvanometer. In the present work, calibrated precision rheostats were used, and settings were made, using different combinations, so as to average out any residual errors in the values of resistance. It is estimated that in this way the values of the inductors used in calibrating the ballistic galvanometer were determined to within 0.01 percent. These values are based on the present international electrical units.

The values of area-turns of the test coils were determined in a similar manner by placing the coils in a solenoid whose constant had been determined by comparison with a standard single-layer solenoid and measuring the mutual inductance. The accuracy of this determination was not so good as that obtained in the measurement of the mutual inductors, because the values of mutual inductance were much smaller. However, this had no important effect on the final result because a systematic error in the observed values of magnetizing force does not affect the saturation value obtained by extrapolation.

One factor which has an important bearing on the accuracy of the measurements is the degree of uniformity of the field in the space immediately adjacent to the specimen, which is occupied by the test coils. This is a function of the distance between the pole pieces, referred to as the gap length. Preliminary investigation of the distribution corresponding to various values of the gap length revealed the fact that the area-turns of the various combinations of test coils were not known to a sufficient degree of precision for this purpose. For this reason, explorations were carried out by means of a single coil so mounted that it could be moved in a radial direction from the surface of the specimen, with its axis always kept parallel to the direction of the field. By using the galvanometer at its maximum sensitivity and moving the coil from various points at measured distances from the surface of the specimen to a point taken as a reference, it was possible to determine the distribution to a satisfactory degree of precision. It was found, as shown in figure 3, that if the gap is too short, the intensity of the field increases with distance from the surface of the specimen. If the gap is too long, the field decreases with radial distance. A gap length of 2.5 cm was found to give a substantially uniform field within a distance of 3 mm from the surface of the speci-

men. Since the inner three coils which were used for the final measurements are all within this distance, the gap length was set at 2.5 cm.

The substantially uniform field in the space occupied by the test coils made it possible to eliminate experimentally the magnetizing

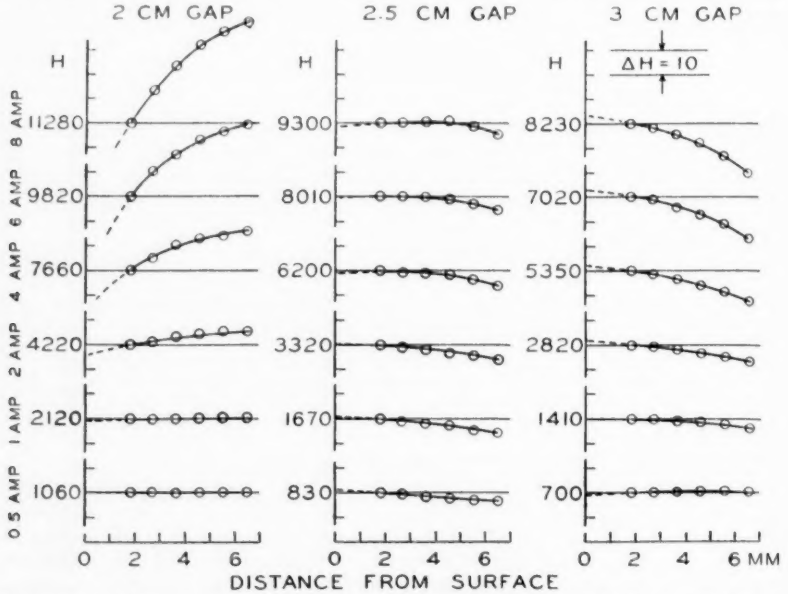

FIGURE 3.—*Influence of gap length on the distribution of the field in a radial direction from the surface of the specimen.*

Note that the observed deviations within 3 mm of the surface for the 2.5-cm gap are not greater than 2 oersteds.

field from the observations and thus avoid errors which might result from subtracting independently observed values of total induction

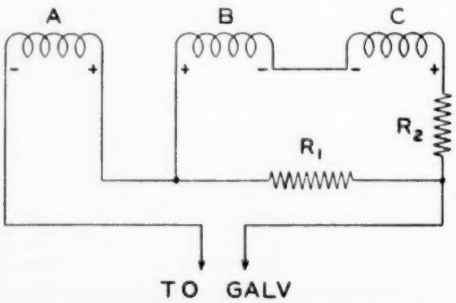

FIGURE 4.—*Connections for adjusting the effective area-turns of the B- and H-coils to equality.*

and magnetizing force. This was done in the manner indicated in figure 4. In the figure, *A*, *B*, and *C* represent the inner three test coils. Coils *B* and *C* are connected in series opposition and so give a measure of the field in the zone between them. The effective area-

turns of this combination can be made equal to the area-turns of coil A by means of resistances R_1 and R_2 connected in the same manner as that used for the comparison of mutual inductances. Preliminary adjustment was made by setting R_1 and R_2 so that

$$\frac{R_1}{R_1+R_2}=\frac{(AN)_A}{(AN)_{BC}},$$

where

$(AN)_A$ = area-turns of coil A,
$(AN)_{BC}$ = area-turns of zone between coils B and C.

The resistances of coils B and C and their leads are included in the value of R_2. Since the coils and leads are of copper, so that their resistance might vary enough with changes in temperature during a run to cause an error in the compensation, the resistance of R_2, including the coils and leads, was measured frequently during the observations, and R_2 was adjusted to compensate for any change which may have occurred.

The compensation was checked experimentally by placing the coils in a uniform field between flat pole pieces in the apparatus. There was no observable deflection of the galvanometer upon reversal of a field of 10,000 oersteds. The galvanometer sensitivity was such that a difference corresponding to 1 oersted, or 0.01 percent, would have been detected.

Since the test coils were only 2 mm long, possible difficulties due to nonuniform distribution of the field in a longitudinal direction were avoided.

The performance of the galvanometer approximates that of a fluxmeter nearly enough for ordinary conditions. However, since the time required to complete the reversal of the magnetizing current in the present apparatus is of the order of 3 seconds, it was found necessary to correct for the effect of the delayed impulse. The amount of the correction was determined by observing the amount by which the deflection due to the reversal of a given current in the primary of the mutual inductor was reduced by connecting the magnetizing coils in series with the inductor primary. This was done for a series of currents in the same range as that used in the final measurements. The correction was found to vary linearly with the reciprocal of the magnetizing force, and this relation was used to calculate the correction to be applied to the saturation value. The correction thus determined is 0.044 kilogauss, or approximately 0.2 percent of the saturation value.

V. TEST SPECIMENS

A specimen was cut from each of 10 ingots and were numbered to correspond with the ingot numbers. One bar was subsequently found to be cracked and one was considered to be excessively porous, so that these specimens were discarded. The bars had been swaged to a diameter of approximately 6.3 mm and were originally about 12 cm long. They were later ground to a diameter of 6.0 mm and cut to a length of 8 cm.

The determination of the cross-sectional areas of the specimens is of considerable importance, because the accuracy of the results depends directly upon the accuracy to which these areas are known.

Mechanical measurements of diameter can be made to the requisite accuracy, but if the specimens are porous there can be no assurance that the area determined from the outside diameter at a given section represents the true area of solid metal at that section. In the light of recent data calculated from lattice constants and of direct measurements on drawn wires presumably free from appreciable porosity, the most probable value for the density of pure iron appears to be 7.874 ± 0.001 g/cm^3. This value was therefore adopted. The observed values for most of the bars are somewhat lower than 7.874 g/cm^3, and this was taken to indicate a slight porosity. The values are given in table 2.

TABLE 2.—*Density*[a] *of specimens* (*in grams per square centimeter*)

	Specimen number—							
	3	6	7	8	12	13	14	18
12 cm, swaged	7.875	7.869	7.873	7.872	7.875	7.867	7.860	7.869
8 cm, ground	[b] 7.869	7.871	7.870	[b] 7.873	7.872	7.867	7.862	7.872

[a] Determined by the Capacity and Density Section of this Bureau, and estimated to be accurate within ± 0.002.
[b] After annealing.

The average cross-sectional area of solid iron can be found from its length, mass, and the true density. However, if the specimen is porous, this gives no indication of the variation of area along the length nor of the exact area at any one place. This variation was investigated by exploring the bars magnetically along their length. By means of small brass rods inserted in the axial holes in the pole pieces, the specimens could be moved along longitudinally by measured amounts as indicated on a scale. By observing the galvanometer deflections when a bar was moved from different positions to a fixed position taken as a reference, it was possible to determine the variation of apparent induction corresponding to a fixed value of magnetizing force. By using the galvanometer at maximum sensitivity, it was possible to observe differences as small as 0.001 kilogauss. The galvanometer was calibrated in terms of the average area, so that the observed variations were proportional to the variations in area.

Since the swaged bars showed large variations in induction, sometimes amounting to as much as 0.5 percent, it was decided to grind the bars in order to have more nearly uniform areas. After the bars were ground, the variations were found to be very much smaller. The curves shown in figure 5 are typical of the results obtained. The magnetic variations after grinding the bars correspond quite closely to the variations in area as determined from measurements of diameter. The relative differences may be attributed for the most part to nonuniformity in distribution of the material due to porosity. Bar 10 still showed so much variation, even after grinding, that it was discarded.

Since it was feasible to explore only 8 cm of the length of the bars, they were cut to that length, and for the calculation of average area only that part was used for which distribution had been determined. The final measurements were made at the middle point of the bars

with the galvanometer calibrated for the average area. The results were then corrected by the percentage that the actual area at the point of observation differed from the average, as indicated by the magnetic exploration data.

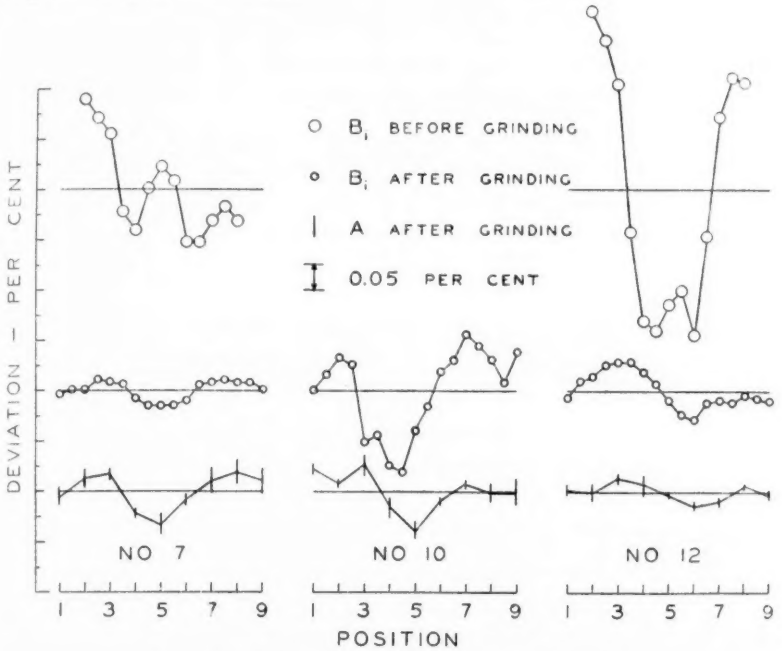

FIGURE 5.—*Typical results of magnetic exploration.*

The lower curves represent the variations in area as determined by measurements of diameter. The upper and middle curves represent the variations in intrinsic induction with position on the bar at a magnetizing force of 5,000 oersteds. The positions indicated are 1 cm apart. Position 5 is the middle of the bar.

VI. FINAL OBSERVATIONS AND RESULTS

Final observations were made at magnetizing forces ranging from 1,500 to 10,000 oersteds. Previous investigators [5, 6] have found that for values of intrinsic induction, B_i, within 1 percent of the saturation value, B_s, the law of approach to saturation is represented by the equation

$$B_i = B_s - b/H.$$

By plotting B_i against $10^4/H$, this law was found to hold for the present results within the experimental error. A typical set of observations plotted in this way is shown in figure 6. In determining the best value of B_s and the slope, b, all of the observed values were utilized by solving the simultaneous equations.

$$\Sigma B_i = NB_s - \Sigma(10^4/H) \times b$$
$$\Sigma(B_i \times 10^4/H) = \Sigma(10^4/H)B_s - \Sigma[(10^4/H)^2] \times b$$

where

ΣB_i=sum of observed values of B_i (kilogausses)
N=number of observed points
B_s=saturation value (kilogausses)
$\Sigma(10^4/H)$=sum of values of $10^4/H$ (H in oersteds)
b=slope of line

It may be noted that none of the observed points departs from the calculated line by as much as 0.01 kilogauss, which was the least count in the observations.

Two independent sets of observations were made on each of the eight specimens. Two of the specimens were then annealed in vacuo, and the observations were repeated, so that in all 10 values were obtained. Specimen 3 was annealed at 865° C for the purpose of relieving the strains produced by swaging. The bar was explored for uniformity after annealing, and the results were practically identical with those for the bar in the swaged condition. Bar 8, on the other hand, gave some very interesting results. The bar was annealed

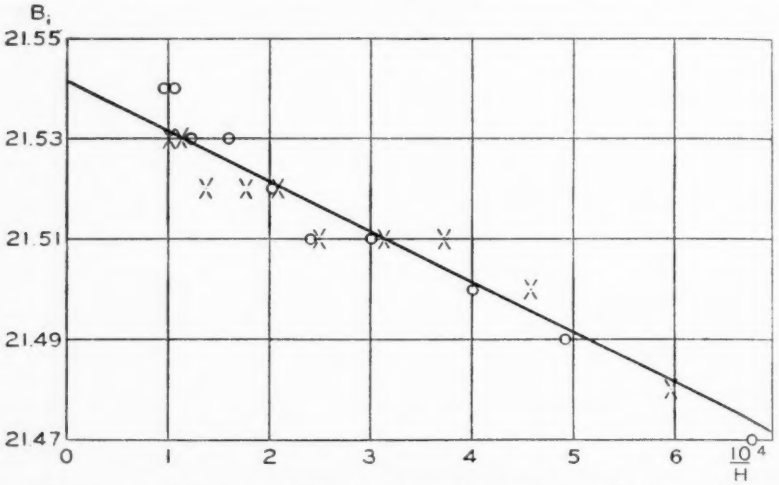

FIGURE 6.—*Method of plotting the observations and extrapolating to the saturation value.*

The points marked by circles are for the first set of observations. Those marked by crosses are for the second set. The position of the line was located by calculation, using all of the observed points

at 1,020° C, with the idea of producing grain growth as well as relieving strains. It was hung from one end in a vertical furnace. The results of magnetic exploration before and after annealing are shown in figure 7. The magnetic exploration of bar 8 after it was annealed indicated that the bar was tapered, and this was confirmed by mechanical measurements of diameter. The high temperature evidently had softened the bar enough to permit a progressive elongation, greatest at the top, which produced a slight taper. It is of interest to note, however, that no appreciable change in the saturation value was brought about by annealing in either case.

The final data and corrected values are given in table 3. In column 1 are given the values of B_s obtained by extrapolation of the observed values of B_i in the manner indicated above. Columns 2, 3, and 4 show the corrections for nonuniformity of area, delayed impulse, and impurities, respectively. In view of the small amounts of the impurities present and the correspondingly small correction necessary, no attempt was made to determine their effects independently. The data given by other investigators were assumed to be sufficiently

accurate for the purpose. The corrections for C, Cu, N, O, and S were based on the work of Steinhaus, Kussmann, and Schoen [6], and the correction for Si from that of Gumlich [3]. The total correction was calculated to be approximately 0.02 percent, or 0.004 kilogauss, which is less than the probable error of the magnetic measurements.

Column 5 gives the final corrected values, showing a mean of 21.578 kilogausses. The percentage deviations from the mean are

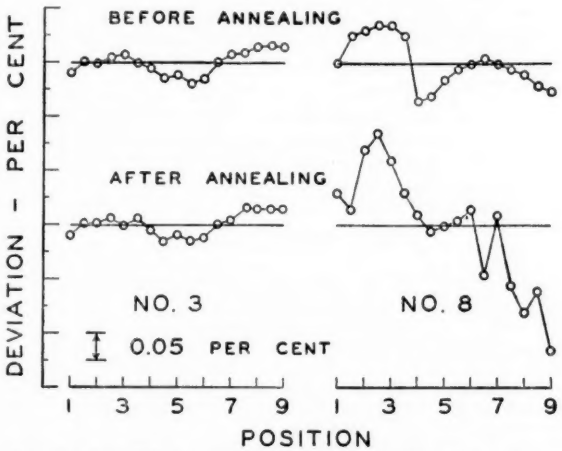

FIGURE 7.—*Effect of annealing on the uniformity of area*

The bars were hung from one end in a vertical furnace and annealed in vacuo. Annealing at 865° C had no appreciable effect on the uniformity of bar 3. Bar 8 was annealed at 1,020° C, which softened the bar enough to allow it to stretch slightly and produce a definite taper. The positions indicated are 1 cm apart on the bars. Position 5 is at the middle.

given in column 6, the numerical average being 0.042 percent and the maximum 0.074 percent.

TABLE 3.—*Final results*

[Column 1. Value by extrapolation of observed points. Column 2. Correction for nonuniformity of area. Column 3. Correction for delayed impulse. Column 4. Correction for effect of impurities. Column 5. Final value. Column 6. Deviation from the mean, percent]

Specimen number	Intrinsic induction (kilogausses)					
	1	2	3	4	5	6
3	21.523	+0.005	+0.044	+0.004	21.576	−0.009
3[a]	21.520	.005	+0.044	+0.004	21.573	−.023
6	21.535	.001	+0.044	+0.004	21.584	+.028
7	21.520	.007	+0.044	+0.004	21.575	−.014
8	21.537	.006	+0.044	+0.004	21.591	+.060
8[a]	21.543	−.001	+0.044	+0.004	21.590	+.056
12	21.541	+.004	+0.044	+0.004	21.593	+.069
13	21.512	.008	+0.044	+0.004	21.568	−.046
14	21.490	.024	+0.044	+0.004	21.562	−.074
18	21.520	.001	+0.044	+0.004	21.569	−.042
Mean					21.578	0.042
Maximum						0.074

[a] Annealed.

In considering the probable accuracy of the final result, the greatest source of uncertainty is the effect of the delayed impulse, for which a correction of 0.2 percent was made. The error in determining this correction is probably not greater than 25 percent of the correction, which leaves an uncertainty, then, of 0.05 percent. The mutual inductance of the inductor was known to 0.01 percent; the measurement of current for calibrating the galvanometer was good to 0.01 percent; the error due to imperfect compensation of the test coils did not exceed 0.01 percent; and the probable experimental error, as calculated from the deviations from the mean, is of the order of 0.01 percent. If the allowance for the effect of impurities should be wrong by 50 percent, the uncertainty would be only 0.01 percent of the total. This gives a total uncertainty of ± 0.1 percent, or ± 0.02 kilogauss, if the errors should be cumulative. However, assuming a random distribution, the probable error is ± 0.05 percent. It seems safe to conclude, therefore, that the saturation value for pure iron at 25° C and based upon a density of 7.874 g/cm^3 is 21.58 ± 0.01 kilogauss.

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Washington, October 3, 1940.

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HYDROTHERMAL AND X-RAY STUDIES OF THE GARNET-HYDROGARNET SERIES AND THE RELATIONSHIP OF THE SERIES TO HYDRATION PRODUCTS OF PORTLAND CEMENT

By E. P. Flint, Howard F. McMurdie, and Lansing S. Wells

ABSTRACT

Isometric tricalcium aluminate hexahydrate, one of the well-established products of hydration of portland cement, forms complete solid solutions with the corresponding ferrite, $3CaO.Fe_2O_3.6H_2O$, with grossularite garnet, $3CaO.Al_2O_3.3SiO_2$, and with andradite garnet, $3CaO.Fe_2O_3.3SiO_2$. Members of this solid-solution series were synthesized by hydrothermal methods, and X-ray determinations were made of their crystal structures. To the series belong: (1) The mineral plazolite, $3CaO.Al_2O_3.2SiO_2.2H_2O$, (2) the major product of hydration of the glass phase in portland cement clinker at elevated temperatures and pressures, and (3) one of the major products of hydration of tetracalcium aluminoferrite.

CONTENTS

	Page.
I. Introduction	14
II. Hydrothermal study	14
1. Preliminary experiments	
(*a*) Reaction of water at elevated temperatures with glasses in the system CaO-$2CaO.SiO_2$-$5CaO.3Al_2O_3$-$4CaO.Al_2O_3.Fe_2O_3$	14
(*b*) Preparation of calcium aluminoferrite hydrates	15
(*c*) Decomposition temperatures of silica-containing calcium aluminoferrite hydrates	18
(*d*) Discussion of results	19
2. Preparation of $3CaO.Al_2O_3.6H_2O$-$3CaO.Fe_2O_3.6H_2O$-grossularite-andradite solid solutions	20
(*a*) Procedure	20
(*b*) Results of analytical and microscopical determinations	21
3. Substitution of other oxides for CaO, Al_2O_3, and Fe_2O_3 in the solid-solution series	23
4. Products of reaction of water with tetracalcium aluminoferrite	23
5. Bearing of results on products of hydration of portland cement	25
6. Summary of hydrothermal study	29
III. X-ray structure studies	26
1. Introduction and methods	26
2. Structure of $3CaO.Al_2O_3.6H_2O$	27
3. The series $3CaO.(Al, Fe)_2O_3.3SiO_2$-$3CaO.(Al, Fe)_2O_3.6H_2O$	29
4. Occurrence of the series as natural minerals	31
5. Summary of X-ray study	32
IV. References	33

I. INTRODUCTION

Although rather extensive investigations have been made on the reactions of the crystalline constituents of portland cement with water, no such study has been reported with respect to the glass phase in cement clinker. In the course of some experiments related to this problem, on the reaction of water at elevated temperatures and pressures with glasses in the quaternary system CaO-Al_2O_3-Fe_2O_3-SiO_2, certain results were obtained which led to an investigation of possible solid solution relationships between the isometric tricalcium aluminate hexahydrate and the isometric tricalcium ferrite hexahydrate recently discovered by Eiger [1].[1] The existence of such solid solutions was confirmed, and it was found that their stability was considerably influenced by the presence of silica.

An extension of the study revealed that silica could replace water in both $3CaO.Al_2O_3.6H_2O$ and $3CaO.Fe_2O_3.6H_2O$, and that the end products of these substitutions are grossularite garnet, $3CaO.Al_2O_3.3SiO_2$, and andradite garnet, $3CaO.Fe_2O_3.3SiO_2$, respectively. Complete solid solutions exist between each of these compounds and the other three. The hydrous members of the series may be termed "hydrogarnets" to indicate their relationship to the naturally occurring garnets.

This investigation is presented in two parts. The first deals with the synthesis of various garnets and hydrogarnets, and the second deals with their structures as revealed by X-ray data.

II. HYDROTHERMAL STUDY

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1. PRELIMINARY EXPERIMENTS

(a) REACTION OF WATER AT ELEVATED TEMPERATURES WITH GLASSES IN THE SYSTEM CaO-$2CaO.SiO_2$-$5CaO.3Al_2O_3$-$4CaO.Al_2O_3.Fe_2O_3$

Small quantities of glasses representative of the composition of various liquid phases at 1,400° C in the system CaO-$2CaO.SiO_2$-$5CaO.3Al_2O_3$-$4CaO.Al_2O_3.Fe_2O_3$ were available from a previous investigation and were used in the preliminary work. Details of the method of preparing these glasses have been given by Lerch and Brownmiller [2]. Half-gram quantities of the finely powdered glasses with 10 ml of CO_2-free water were placed in steel bombs of 40-ml capacity, and the bombs were then heated at constant temperature (±5 degrees C) in electric furnaces for several days. The apparatus and procedure were the same as those described in a previous publication [3]. After the completion of the heating period, the products were removed from the bombs, washed with alcohol and ether, and dried over calcium chloride in a desiccator. The results obtained from treatment of glasses of various compositions are listed in table 1.

[1] Numbers in brackets indicate the literature references at the end of this paper.

TABLE 1.—*Results of treating* CaO-Al_2O_3-Fe_2O_3-SiO_2 *glasses with water at elevated temperatures*

Experiment number	Oxide composition of the glasses				Temperature	Time	Crystalline phases in product
	CaO	Al_2O_3	Fe_2O_3	SiO_2			
	%	%	%	%	°C	Days	
1 [a]	58.3	33.0	0.0	8.7	250	6	90% isometric phase, $n=1.615$.
2	56.7	30.3	5.0	8.0	200	5	80% isometric phase, $n=1.625$; scarce hematite; no $Ca(OH)_2$; 10% unreacted glass.
3 [b]	54.8	22.7	16.5	6.0	200	4	80% isometric phase, $n=1.655$; 5 to 10% hematite; 5% $Ca(OH)_2$.
4	53.1	17.8	23.7	5.5	200	5	70% isometric phase; $n=1.655$; 10 to 15% hematite; 10% $Ca(OH)_2$.
5	58.1	23.5	18.4	0.0	200	9	30 to 40% isometric phase, $n=1.625$.
6	56.3	17.0	26.7	.0	200	7	20 to 30% isometric phase, $n=1.65$.
7	54.5	11.0	34.4	.0	175	9	20 to 30% isometric phase, $n=1.67$.

[a] Composition of liquid at invariant point $3CaO.Al_2O_3$, $2CaO.SiO_2$, $3CaO.SiO_2$ in system CaO-Al_2O_3-SiO_2.
[b] Composition of liquid at quaternary eutectic $3CaO.SiO_2$, $2CaO.SiO_2$, $3CaO.Al_2O_3$, $4CaO.Al_2O_3.Fe_2O_3$ in system CaO-Al_2O_3-Fe_2O_3-SiO_2.

The predominant phase obtained in experiments 1 to 4 consisted of isotropic crystals, frequently of rectangular outline but often appearing to retain the shapes of the original glass fragments. These aggregates exhibited closely spaced longitudinal striations. The index of refraction of the isotropic phase increased from 1.615, in the product from the Fe_2O_3-free glass, to 1.655, in the product of experiment 4. This change in refractive index was accompanied by a deepened yellow color of the crystals.

Because the refractive indices of this phase were intermediate between those of $3CaO.Al_2O_3.6H_2O$, $n=1.605$, and the isomorphous compound $3CaO.Fe_2O_3.6H_2O$, $n=1.710$, it seemed probable that the crystals might represent solid solutions of these two compounds. Experiments 5, 6, and 7 record attempts to prepare members of such a solid-solution series. The glasses used contained CaO, Al_2O_3, and Fe_2O_3 in the molar proportions 9:2:1, 6:1:1, and 9:1:2. If but one phase were formed in the hydration of these glasses, the resulting products would be intermediate between $3CaO.Al_2O_3.6H_2O$ and $3CaO.Fe_2O_3.6H_2O$ in composition. Similar treatments in the bombs gave much smaller amounts of the isometric phase than had been obtained from the glasses containing silica. The balance of the products consisted of hematite, calcium hydroxide, and considerable poorly crystallized unidentified material. Apparently the presence of silica in the glasses of experiments 1 to 4 helped to stabilize the isometric phase.

Other CaO-Al_2O_3-Fe_2O_3 glasses were prepared, using B_2O_3 as a flux, but on hydration these gave a highly birefringent material as the primary phase and none of the isometric crystals. Another method of preparation therefore was sought.

(b) PREPARATION OF CALCIUM ALUMINOFERRITE HYDRATES

Eiger [1] prepared $3CaO.Fe_2O_3.6H_2O$ by treating colloidal hydrated ferric oxide with a lime solution for 6 weeks, and he obtained in this way a mixture of isometric crystals of refractive index 1.710 and hexagonal crystals of indices 1.61 to 1.65. The isometric $3CaO.Al_2O_3.6H_2O$ may also be obtained at room temperature, but is like-

wise usually accompanied by considerable amounts of the hexagonal form of hydrated calcium aluminate [4], unless sufficient time is allowed for transformation of the hexagonal to the isometric form, a process that usually requires several months. A product made in this way is shown in figure 1. However, if the preparation is carried out at higher temperatures (60° to 100° C.), the isometric aluminate crystallizes without any of the hexagonal form [5]. Since, in this study, preparations were desired which would be free from hexagonal ferrite or aluminate, a method was adopted wherein crystallization was brought about at 100° C.

The procedure involved the very slow addition of a dilute acidified solution of iron and aluminum chlorides to a large volume of boiling calcium hydroxide solution. Samples of iron and aluminum of high purity and ignited reagent quality calcium carbonate were the original materials. Sufficient iron and aluminum were used in all cases to give 3 g of each hydrate. In each experiment the required quantities of the two metals were placed in a small beaker, dissolved in 10 to 15 ml of 6 *N* HCl, and any ferrous iron was oxidized by the addition of hydrogen peroxide. After evaporation to dryness to remove excess HCl, the mixture of ferric and aluminum chlorides was taken up in 100 ml of CO_2-free water containing 2 ml of concentrated HCl. This solution was then added over an interval of 8 to 10 hours to 5½ liters of boiling lime suspension (1.15 g of CaO per liter). The lime suspension was contained in a 6-liter flask fitted with a rubber stopper carrying a reflux condenser and a dropping funnel with a constricted tip. Protection from atmospheric CO_2 was provided by soda-lime tubes. The solution in the flask was kept boiling vigorously on a hot plate. It was found necessary to add the $FeCl_3$-$AlCl_3$ solution in very small droplets at the rate of only 10 to 15 ml per hour in order to prevent the precipitation of ferric hydroxide by the lime solution. After all of the chloride solution had been added, boiling was continued for an additional half hour. The resulting mixture was cooled to room temperature and agitated until any calcium hydroxide crystals present had been dissolved. The product was then filtered off, washed with alcohol and ether, and dried overnight in a calcium chloride desiccator. Chemical analyses and index of refraction measurements are given in table 2.

TABLE 2.—*Compositions and indices of refraction of hydrated calcium aluminoferrite solid solutions*

Sample number	Composition by analysis					Molar ratios of preparations						Index of refraction
	CaO	Al_2O_3	Fe_2O_3	SiO_2	H_2O	CaO	Al_2O_3	Fe_2O_3	SiO_2	H_2O	$H_2O+2SiO_2$	
	%	%	%	%	%							
1	44.35	26.38	------	1.06	27.81	3.06	------	1.00	0.07	5.97	6.11	1.607
2	43.12	24.06	2.37	6.28	23.97	3.07	0.94	0.06	.41	5.31	6.13	1.618
3	41.56	15.63	12.83	5.36	24.56	3.18	.66	.34	.38	5.83	6.59	1.642
4	40.72	11.85	18.36	6.37	22.52	3.15	.50	.46	.46	5.42	6.34	1.665
5	38.52	7.52	26.30	3.34	23.78	2.88	.31	.69	.23	5.52	5.98	1.675
6	40.22	7.97	24.65	4.16	23.04	3.09	.34	.66	.30	5.50	6.10	1.678
7	38.28	------	35.55	5.13	20.56	3.07	------	1.00	.38	5.24	6.00	1.720
8	38.50	------	35.19	5.54	20.70	3.12	------	1.00	.42	5.34	6.18	1.723
9	38.19	------	35.27	7.11	19.79	3.08	------	1.00	.54	4.97	6.05	1.730
10	40.03	------	32.16	6.34	21.83	3.54	------	1.00	.52	6.01	7.05	1.710

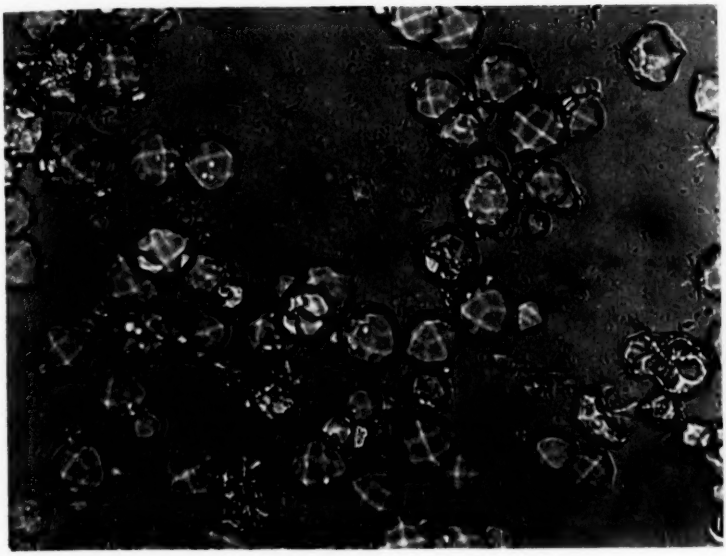

FIGURE 1.—*Icositetrahedral form of* $3CaO.Al_2O_3.6H_2O$.
Magnification ×250.

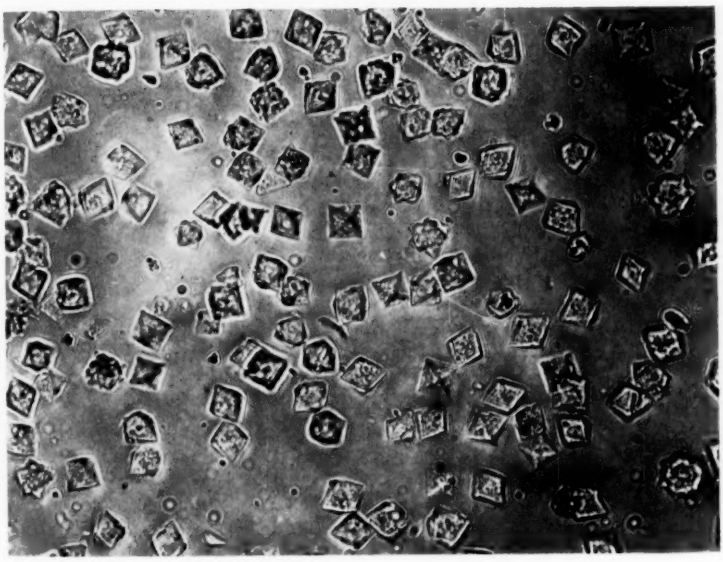

FIGURE 2.—*Preparation 2, table 2.*
Magnification ×400.

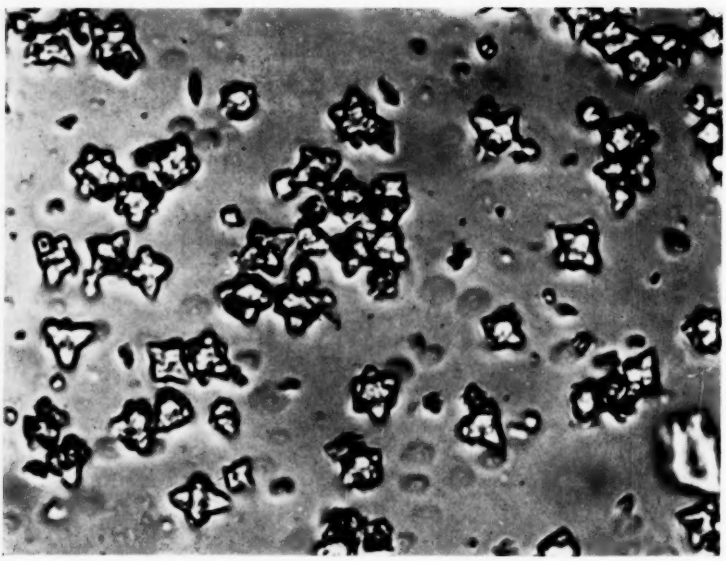

FIGURE 3.—*Preparation 7, table 2.*
Magnification ×1300.

Microscopical examinations of the products indicated a purity of 95 percent or better, the preparations being made up of well-developed octahedral crystals. None of the other crystal habits reported by other writers (cubes, rhombic dodecahedrons, icositetrahedrons, etc.) of $3CaO.Al_2O_3.6H_2O$ was observed. A photomicrograph of a typical preparation is shown in figure 2. The preparations toward the aluminate end of the series gave the best developed crystals, and the crystal size decreased as their iron content increased. Toward the ferrite end of the series the octahedral faces of the crystals were not completely developed, and exhibited the cross-like appearance shown in figure 3. The iron-containing products were of a light-yellow color.

Although no silica or hydrated calcium silicate could be detected microscopically in the products, the analyses in table 2 show each sample to be contaminated by 1 to 7 percent of SiO_2. Furthermore, the water contents (H_2O/R_2O_3) of the preparations are consistently lower than the theoretical value ($H_2O/R_2O_3=6$). However, if the molar ratio of $(H_2O+2SiO_2)/R_2O_3$ is calculated, values in better accord with theory are obtained, as may be seen in the table. It will be noted also that all but one of the silica-containing $3CaO.Fe_2O_3.6H_2O$ preparations have refractive indices slightly higher than the 1.710 reported by Eiger [1].

Various expedients were tried in attempts to eliminate the contamination by silica. Experiments were made using copper and iron reaction vessels, but the products thereby obtained were all badly contaminated with hydrous iron oxide, no matter how slowly the iron-containing solution was added. The same condition resulted when a silver-lined glass flask was used. Thus, as in the case of the treatment of the CaO-Al_2O_3-Fe_2O_3-SiO_2 glasses with water, it is indicated that the presence of silica helps to stabilize the calcium aluminoferrite hydrates.

Glass containers of various compositions were tried, but none was found having complete resistance to lime solution. Other experiments were made wherein the reaction period in the glass flask was reduced to 3 hours. This could be accomplished without precipitation of ferric hydroxide if the iron-aluminum chloride solution was added to a rather heavy lime suspension containing about 10 g of CaO in excess of that used previously. After cooling the mixture to room temperature, the excess lime was removed by diluting with sufficient CO_2-free water. However, it was found that the preparations were not improved by this treatment, as they still contained 4 to 5 percent of silica.

One preparation (No. 10, table 2) of the compound $3CaO.Fe_2O_3.6H_2O$ was attempted in a container of dense unglazed porcelain. Analysis showed 6.34 percent of silica, and the composition corresponded to $3.54\ CaO{:}1.00Fe_2O_3{:}0.52SiO_2{:}6.01H_2O$. This preparation differs from the others listed in table 2 in showing considerable contamination by fine-grained material of low birefringence, which may have been hydrated calcium silicate. However, it is included here because a determination of the unit-cube size of the isometric constituent in Section III of this paper showed very close agreement with the estimated theoretical unit-cell value of $3CaO.Fe_2O_3.6H_2O$.

When ferric chloride solution is added to limewater at room temperature a calcium chloroferrite, $3CaO.Fe_2O_3.CaCl_2.10H_2O$, is formed. At room temperature this compound goes over slowly to $3CaO.Fe_2O_3.6H_2O$. Thus, a chloroferrite precipitate allowed to stand at room temperature for 95 days in contact with its solution was about 50 percent converted to the isometric compound. This sample contained 0.83 percent of SiO_2. Another chloroferrite preparation, which was filtered shortly after precipitation, and hence contained negligible silica, was placed in contact with dilute lime solution (0.626 g of CaO/liter) and maintained at 60° C with frequent shaking. After 2 weeks, it was completely transformed to the isometric compound. The product was found to contain 6.85 percent of SiO_2 taken up from the glass container during this period.

(c) DECOMPOSITION TEMPERATURES OF SILICA-CONTAINING CALCIUM ALUMINOFERRITE HYDRATES

To determine the temperatures at which members of the series break down in contact with solution, 0.2- to 0.3-g samples of some of the preparations listed in table 2 were heated in the bombs with 10 ml of a dilute lime solution (0.2 g of CaO per liter) at various temperatures. The decomposition temperature was assumed to be that above which

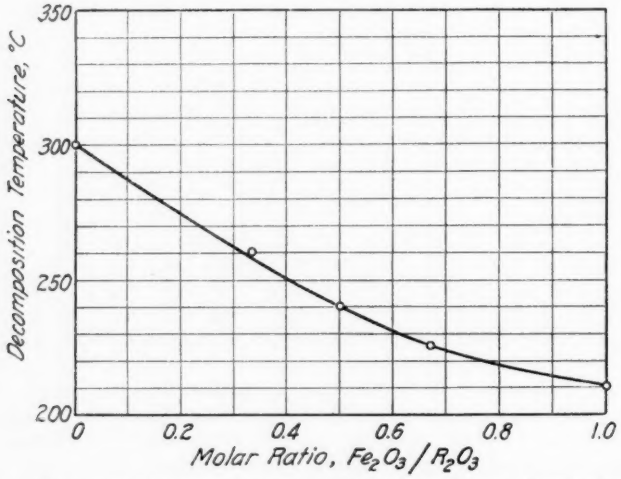

FIGURE 4.—*Decomposition temperatures of hydrated calcium aluminoferrites containing silica.*

appreciable quantities of hematite or gibbsite, as well as calcium hydroxide, appeared. The results are listed in table 3. Figure 4 summarizes these data, the temperatures plotted being the average of the two limiting temperatures, except in the case of $3CaO.Al_2O_3.6H_2O$, where it was taken as 300° C.

TABLE 3.—*Decomposition temperatures of hydrated calcium aluminoferrites*

Sample number	Molar ratio Al_2O_3/Fe_2O_3	Temperature	Time	Extent of decomposition
		° C	Days	
1[a]	1:0	290	14	None.
		300	27	Very slight, but all crystals etched.
		320	27	Partial.
		420	6	Complete.
3	2:1	250	34	None.
		270	41	Slight.
		290	48	Almost complete.
		330	14	Do.
4	1:1	230	44	None.
		250	35	Partial.
		260	8	Do.
		280	8	Almost complete.
6	1:2	220	29	None.
		230	22	Partial.
8	0:1	150	77	None.
		200	20	Do.
		220	13	Slight.
		230	8	Partial.

[a] Samples are numbered to correspond with the designations used in table 2.

In spite of the long digestion periods below the decomposition temperatures, the crystal size of the hydrates was not greatly increased.

As will be shown later, the decomposition temperatures are influenced considerably by the presence of silica in the preparations. The fact that figure 4 is nearly a smooth curve probably is caused by the presence of roughly the same amounts of silica in the preparations, except in the $3CaO.Al_2O_3.6H_2O$ product.

(d) DISCUSSION OF RESULTS

The data in tables 1 and 2 indicate that $3CaO.Al_2O_3.6H_2O$ and $3CaO.Fe_2O_3.6H_2O$ form a complete series of solid solutions. However, it is evident from the following considerations that silica is also a factor in the solid solutions as follows:

1. The isometric product obtained from a glass containing 8.7 percent of SiO_2 but no Fe_2O_3 (experiment 1, table 1), has a refractive index appreciably higher than that of ordinary $3CaO.Al_2O_3.6H_2O$.

2. The mineral plazolite, $3CaO.Al_2O_3.2SiO_2.2H_2O$, [2] [7] crystallizes in the isometric system with a refractive index of 1.675 [8] intermediate between $n=1.605$ for $3CaO.Al_2O_3.6H_2O$ and $n=1.735$ for grossularite garnet, $3CaO.Al_2O_3.3SiO_2$. Winchell [9] has pointed out the similarity between plazolite and grossularite. The formula of plazolite can be accounted for by assuming that two molecules of H_2O have replaced one molecule of SiO_2 in grossularite, or that two molecules of SiO_2 have replaced four molecules of H_2O in $3CaO.Al_2O_3.6H_2O$.

3. Although no natural ferrite corresponding to plazolite is known, the presence of quantities of SiO_2 up to 7.1 percent in the preparations of $3CaO.Fe_2O_3.6H_2O$ listed in table 2 points to the possibility of

[2] The original formula, $3CaO.Al_2O_3.2SiO_2.2(CO_2, H_2O)$, given for plazolite is incorrect, the carbonate content of the samples analyzed being due to the presence of small amounts of calcite. (Personal communication from W. F. Foshag).

analogous solid solution between $3CaO.Fe_2O_3.6H_2O$ and andradite garnet, $3CaO.Fe_2O_3.3SiO_2$.

4. The preparations listed in table 2, with the exception of No. 10, have a water content of less than 6 moles. This can be accounted for by the assumption, as in the case of plazolite mentioned above, that 2 parts of H_2O were replaced by 1 part of SiO_2.

5. All attempts to obtain stable iron-containing preparations, except in the glass or porcelain containers which served as sources of silica during the reaction, were unsuccessful. Evidently the isometric calcium ferrite or aluminoferrite hydrates are unstable in the absence of a certain amount of silica in solid solution.

6. Numerous analyses of naturally occurring garnets prove the existence of a complete series of solid solutions between grossularite, $3CaO.Al_2O_3.3SiO_2$, and andradite, $3CaO.Fe_2O_3.3SiO_2$ [10].

Confirmation of the above points was obtained in the X-ray study, the results of which will be presented in another section of this paper.

On the basis of the available evidence, the solid solution relationships of $3CaO.Al_2O_3.6H_2O$ with Fe_2O_3 and SiO_2 may, therefore, be tentatively formulated as follows:

$$\begin{array}{ccc} 3CaO.Al_2O_3.6H_2O & — & 3CaO.Al_2O_3.3SiO_2 \\ | & & | \\ 3CaO.Fe_2O_3.6H_2O & — & 3CaO.Fe_2O_3.3SiO_2, \end{array}$$

each end member being capable of forming complete mixed crystals with the other three members. Each part of Fe_2O_3 displaces 1 part of Al_2O_3, while 1 part of SiO_2 substitutes for 2 parts of H_2O.

2. PREPARATION OF $3CaO.Al_2O_3.6H_2O$-$3CaO.Fe_2O_3.6H_2O$-GROSSULARITE-ANDRADITE SOLID SOLUTIONS

(a) PROCEDURE

In order to obtain homogeneous materials for hydrothermal treatment, glasses of the desired compositions were prepared from reagent quality calcium carbonate, alumina, ferric oxide, and purified silica gel (0.03 percent of nonvolatile residue on ignited basis). The mixtures were thoroughly ground and given a preliminary ignition at 1,200° C. All melts were prepared in a platinum resistance furnace. Those having liquidus temperatures of 1,400 to 1,450° C. were made in 5-g quantities in a furnace used for making experimental glasses; the remainder, in quantities of 0.5 to 1 g, were wrapped in platinum foil and quenched from the higher temperatures. The melts were held above the liquidus temperatures for 15 minutes before quenching. Glasses of uniform index and free from birefringent material were thus obtained.

The oxide ratios of glasses prepared and the temperatures from which the liquids were quenched are given in table 4. As a check on the accuracy of the calculated compositions, glasses 13, 14, 17, 18, and 19 were analyzed, with the results shown in table 4.

TABLE 4.—*Glasses prepared for study of solid solution relationships in the system* $3CaO.R_2O_3.3SiO_2$-$3CaO.R_2O_3.6H_2O$

Sample number	Calculated oxide ratios of glasses				Temperature of quenching	Compositions of glasses by analysis								
						Oxide analysis					Oxide ratios [a]			
	CaO	Al_2O_3	Fe_2O_3	SiO_2		CaO	Al_2O_3	Fe_2O_3	FeO	SiO_2	CaO	Fe_2O_3	Al_2O_3	SiO_2
					°C	%	%	%	%	%				
11	3	1	-----	0.5	1,520	-----	-----	-----	-----	-----	-----	-----	-----	-----
12	3	1	-----	1	1,540	-----	-----	-----	-----	-----	-----	-----	-----	-----
13	3	1	-----	2	1,540	43.15	25.25	-----	-----	31.62	3.11	-----	0.94	2.13
14	3	1	-----	3	1,410	37.27	22.75	-----	-----	39.95	3.00	-----	1.00	2.94
15	3	0.5	0.5	1.5	1,540	-----	-----	-----	-----	-----	-----	-----	-----	-----
16	3	.5	.5	2	1,400	-----	-----	-----	-----	-----	-----	-----	-----	-----
17	3	.5	.5	3	1,450	35.30	10.86	15.68	0.99	37.25	2.93	0.49	0.51	2.89
18	3	-----	1	2	1,410	37.51	-----	35.02	.80	26.78	2.97	1.00	-----	1.98
19	3	-----	1	3	1,400	33.11	-----	28.61	3.00	35.24	2.96	1.00	-----	2.94

[a] Oxide ratios if FeO is calculated to Fe_2O_3.

The appearance of ferrous oxide in glasses 17, 18, and 19 introduces some uncertainty as to their suitability for hydrothermal treatment, but the amount of reduction is perhaps not sufficiently large to be significant except in the case of glass 19.

The preparation of a number of other glasses was attempted, but it was found that the melting points of the compositions ($3CaO.Fe_2O_3.SiO_2$, $6CaO.2Fe_2O_3.3SiO_2$, and $6CaO.Al_2O_3.Fe_2O_3.2SiO_2$) were above the temperature range of the furnace.

As before, 0.5-g quantities of the finely powdered glasses were treated in the bombs with 5 to 10 ml of water at various temperatures and for different lengths of time. The products were washed with alcohol and ether and dried in a desiccator over calcium chloride. Ignition-loss determinations, microscopical examinations, and X-ray patterns were then made of the products.

(b) RESULTS OF ANALYTICAL AND MICROSCOPICAL DETERMINATIONS

Table 5 summarizes the results of the hydrothermal treatment of the various glasses. As the table indicates, in the five cases in which more than one temperature was used, certain temperatures are more effective than others in bringing about crystallization. Above or below the optimum temperature, crystallization is either very slow or decomposition to more than one product occurs.

TABLE 5.—*Products of hydrothermal treatment of glasses in the system* $3CaO.R_2O_3.3SiO_2$-$3CaO.R_2O_3.6H_2O$

Sample number	Oxide ratio of glasses				Temperature of good crystallization	Pressure	Time	H_2O/R_2O_3 in product		Other temperatures tried
	CaO	Al_2O_3	Fe_2O_3	SiO_2				Theoretical	Actual	
					°C	*atm*	*Days*			°C
11	3.00	1.00	-----	0.50	200	15	14	5	4.73	None
12	3.00	1.00	-----	1.00	250	39	20	4	3.83	None
13	3.11	0.94	-----	2.13	350	163	13	2	2.27	300
14	3.00	1.00	-----	2.94	500	420	6	0	0.59	300, 400, 600
15	3.00	0.50	0.50	1.50	300	85	28	3	2.55	None
16	3.00	.50	.50	2.00	200	15	28	2	2.15	None
17	2.93	.51	.49	2.89	500	330	17	0	0.55	300, 400, 600
18	2.97	-----	1.00	1.98	150	5	17	2	2.10	200, 350, 400
19	2.96	-----	1.00	2.94	500	420	11	0	0.30	300, 400

The preparations consisted, in all cases, of very small crystals of the isometric phase, the refractive index of which increased with increase in the SiO_2 content of the treated glasses, both in the Al_2O_3 and Fe_2O_3 series. The refractive indices of the products from experiments 13 and 14 checked approximately those of plazolite and grossularite, respectively, but, in general, the refractive indices of the crystals could not be accurately determined because of their small size.

Departure of the water contents of the preparations from theoretical values is caused partially by the fact that in some cases a small percentage of unreacted glass remained after the hydrothermal treatment. Also, most of the products contained a few percent of poorly crystallized material, indicating that the action of the glass with water

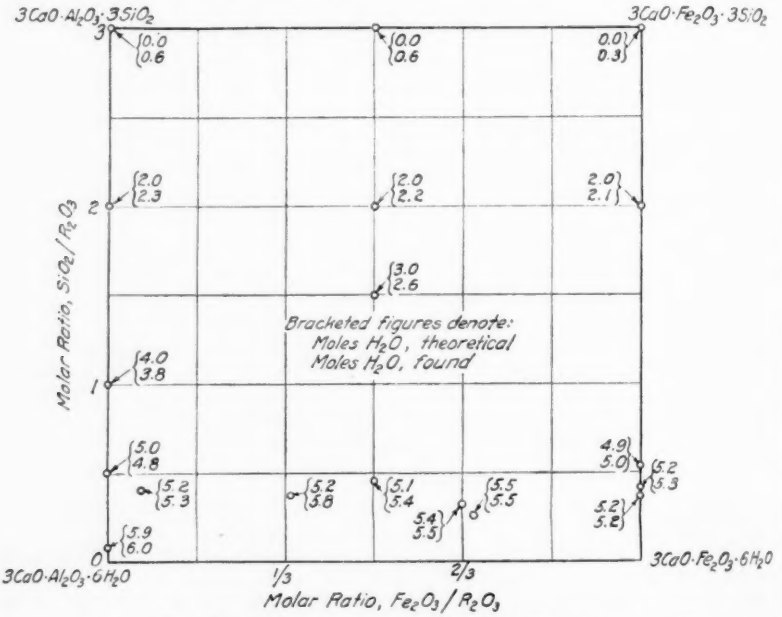

FIGURE 5.—*Compositions prepared in the solid-solution series* $3CaO.R_2O_3.6H_2O$-$3CaO.R_2O_3.3SiO_2$.

was not completely uniform. In the case of the iron-containing glass, some of the difficulty is probably caused by the presence of FeO, although the percentage of this constituent seems to be considerably reduced by the hydrothermal treatment. Thus the andradite garnet preparation (No. 9, table 5) contained only 0.4 percent of FeO, although 3.0 percent of FeO had been present in the original glass.

Figure 5, constructed from data in tables 2 and 4, illustrates the solid-solution relationships of the two garnets and the aluminate and ferrite hydrogarnets. The hydrate of any composition within the rectangle consists of a single isometric phase containing between 0 and 6 moles of H_2O per mole of R_2O_3.

3. SUBSTITUTION OF OTHER OXIDES FOR CaO, Al_2O_3, AND Fe_2O_3 IN THE SOLID-SOLUTION SERIES

In the hope of obtaining preparations better suited for crystallographic studies than $3CaO.Al_2O_3.6H_2O$ or $3CaO.Fe_2O_3.6H_2O$, synthesis of analogous compounds in which the CaO is replaced by MgO, MnO, BaO, and SrO, and the Al_2O_3 or Fe_2O_3 by Cr_2O_3 was attempted. As before, the method involved the very slow addition of solutions of the chlorides of aluminum and chromium to boiling solutions of calcium, barium, or strontium hydroxides. For preparation of the magnesium and manganese compounds, solutions of the chlorides of these two metals were added slowly to boiling solutions of sodium aluminate. In no case was a material obtained bearing any similarity to the isometric aluminate or ferrite hydrates. Brandenberger [6], however, has reported the existence of an isometric compound $3SrO.Al_2O_3.6H_2O$, but he does not state how it was prepared.

A number of glasses having compositions corresponding to possible garnets were also made up and treated with water in the bombs at 500° C, 400 atmospheres, for periods of 1 to 3 weeks. The products from $3BaO.Al_2O_3.3SiO_2$ and $3SrO.Al_2O_3.3SiO_2$ showed extensive decomposition to $Ba(OH)_2$ and $Sr(OH)_2$ and apparently contained none of the isometric phase. The glass $3MgO.Al_2O_3.3SiO_2$ gave a finely divided, apparently heterogeneous product, none of the material having a refractive index as high as that of pyrope, the corresponding garnet ($n=1.725$). A glass of equimolar proportions of $3CaO.Al_2O_3.3SiO_2$ and $3MgO.Al_2O_3.3SiO_2$ gave a product containing much birefringent material.

4. PRODUCTS OF REACTION OF WATER WITH TETRACALCIUM ALUMINOFERRITE

The reaction of tetracalcium aluminoferrite with a large excess of water appears to be somewhat different from that which occurs when the ferrite is mixed with only enough water to form a paste.

In the experiments with a large excess of water, 100 g of $4CaO.Al_2O_3.Fe_2O_3$ was shaken with 2 liters of CO_2-free water for various lengths of time, the solutions filtered, and analyses for dissolved lime and alumina made on 200-ml aliquots of the filtrates. The concentrations (expressed as g of CaO and Al_2O_3 per liter) in the resulting solutions, which contained no Fe_2O_3, are shown in figure 6.

The concentration of the alumina in solution increased rapidly with the time of shaking, and reached a maximum in 30 minutes, after which it decreased gradually. A similar change occurred with the lime in solution but differed from that of the alumina in that the concentrations were higher. This is in contrast to the mechanism of the reaction of water on the calcium aluminates and calcium aluminate cements, where the concentration of the alumina in solution in the early stages greatly exceeds that of the lime and becomes in some instances over 2 g of Al_2O_3 per liter [4].

All of these solutions were metastable and gave "silky" precipitates on standing. After 3 months, the precipitates were examined microscopically. They consisted of the hexagonal forms of hydrated calcium aluminate with, in most cases, smaller proportions of isometric $3CaO.Al_2O_3.6H_2O$ of normal index, $n=1.605$.

One of the mixtures of $4CaO.Al_2O_3.Fe_2O_3$ and water was allowed to stand for 10 years at room temperature, with occasional shaking. Analysis of this solution showed but a trace of alumina. The lime in solution was 1.087 g of CaO per liter, slightly less than that of a saturated lime solution. This increase in concentration of lime was accompanied by the disappearance of the hexagonal forms of hydrated calcium aluminate and of the anhydrous phase. The solid residue was a mixture of isometric crystals and finely divided reddish material. The bulk of the isometric crystals had the normal refractive index of $3CaO.Al_2O_3.6H_2O$. A relatively small proportion possessed a higher

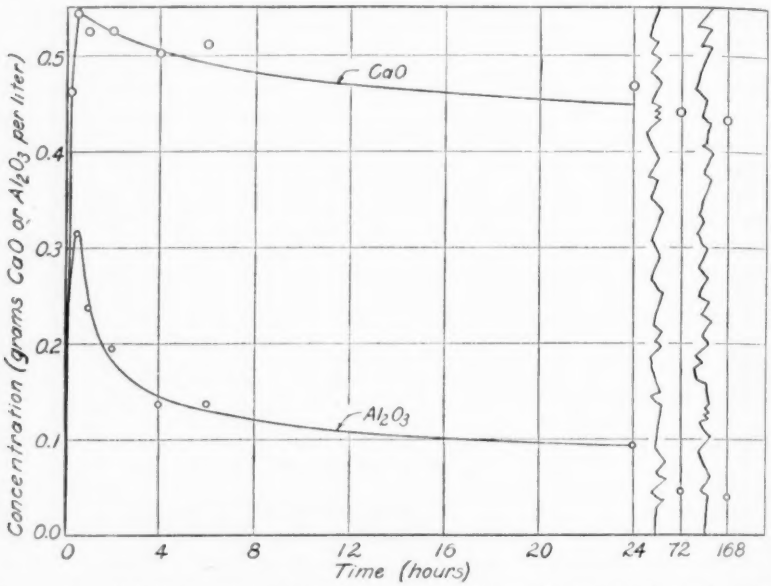

FIGURE 6.—*Solutions obtained by shaking tetracalcium aluminoferrite with water.*

index of refraction, with a maximum value of about 1.637. An X-ray determination of the unit-cube size of the product checked the value of pure $3CaO.Al_2O_3.6H_2O$. The quantity of the material of higher refractive index was too small to have any apparent effect on the pattern.

The reaction of tetracalcium aluminoferrite with a large excess of water appears, therefore, to involve the formation of supersaturated solutions containing CaO and Al_2O_3 but no Fe_2O_3, the precipitation of the hexagonal forms of hydrated calcium aluminate, and the gradual transformation of these forms into the isometric hydrated aluminate. Since most of the isometric crystals have the index of refraction and the unit-cube size of $3CaO.Al_2O_3.6H_2O$, practically all of the Fe_2O_3 from the original $4CaO.Al_2O_3.Fe_2O_3$ must be contained in the accompanying finely divided reddish material.

In order to investigate the reaction when only a limited amount of water is present, a paste of 10 g of tetracalcium aluminoferrite and 5 g of water was stored in a sealed glass vial for 6 days. Microscopical examination of the mixture showed the presence of about 20 percent

of unhydrated $4CaO.Al_2O_3.Fe_2O_3$ with the alteration products consisting of a mixture of reddish amorphous material and of isometric crystals with index of 1.63 to 1.64.

Because of the increased refractive index, it appears probable that this material contained some Fe_2O_3 in solid solution. As is explained in detail later in this paper, an increased unit cell results from the replacement, in whole or in part, of the Al_2O_3 by Fe_2O_3 in this structure, and the increase is in direct proportion to the amount of Al_2O_3 replaced. An X-ray powder pattern was made of this material, and a measurement of the unit cell indicated an increased size, this in turn confirming the result of the determination of the refractive index.

The pure $3CaO.Al_2O_3.6H_2O$ has a unit-cube size of 12.56 A, while $3CaO.Fe_2O_3.6H_2O$ has a cube of 12.74 A. The hydrate prepared from $4CaO.Al_2O_3.Fe_2O_3$ had a cell size of 12.60 A, thus 0.04 A larger than that of the pure calcium aluminate hydrate.

Lerch and Bogue [11] likewise found that the isometric phase from $4CaO.Al_2O_3.Fe_2O_3$ pastes had a refractive index of 1.640. Their failure to find any displacement in its X-ray pattern is probably due to the fact that the shift is very small and not easily detected by the camera which they used.

A sample of dry $4CaO.Al_2O_3.Fe_2O_3$ steamed in an autoclave at 150° C for 6 days still contained a considerable quantity of the anhydrous ferrite. The isometric product, as before, had a refractive index of 1.63 to 1.64 and a unit-cube size, calculated from the X-ray pattern, of 12.60 A. The index of refraction of the isometric phase is somewhat higher than the value reported by Mather and Thorvaldson [12] for the isometric grains obtained by steaming $4CaO.Al_2O_3.Fe_2O_3$ at 150° C and other temperatures.

In another experiment, 2 g of $4CaO.Al_2O_3.Fe_2O_3$ was treated with 5 ml of water at 225° C for 3 weeks. No unhydrated $4CaO.Al_2O_3.Fe_2O_3$ remained in the product. The index of refraction of the isometric phase showed approximately the same variation as before, and a determination of the unit-cube size gave a value of 12.62 A.

5. BEARING OF RESULTS ON PRODUCTS OF HYDRATION OF PORTLAND CEMENT

The foregoing results suggest that the hydration products of the tetracalcium aluminoferrite and glass of portland cement belong to the solid-solution series described in this paper. Whether or not similar hydrates are formed during the reaction with water of the silicates and aluminate compounds which may be in portland cement has not been proved. However, some recent work reported by Büssem [13] indicates that this may be the case.

According to Büssem, a product having the composition $3CaO.Al_2O_3.2SiO_2.xH_2O$ (cf. plazolite, $3CaO.Al_2O_3.2SiO_2.2H_2O$) is obtained in the reaction of limewater on dehydrated kaolin and also when $3CaO.SiO_2$ and $3CaO.Al_2O_3$ are precipitated in water. On account of the finely divided state of his product, it was impossible to ascertain microscopically whether it consisted of one, or more than one, phase. On heating the material to 1,200° C, it was converted to a mixture of gehlenite ($2CaO.Al_2O_3.SiO_2$) and pseudowollastonite ($CaO.SiO_2$). This was advanced by Büssem as proof that the original hydrate was a mixture of hydrated gehlenite ($2CaO.Al_2O_3.SiO_2.xH_2O$)

and hydrated tricalcium disilicate. However, it would seem at least equally permissible to assume that the original material consisted of a single phase, possibly related to the mineral plazolite, which decomposed according to the equation: $3CaO.Al_2O_3.2SiO_2.xH_2O = 2CaO.Al_2O_3.SiO_2 + CaO.SiO_2 + xH_2O$.

The possible formation of hydrated calcium aluminosilicate during the reaction of water with portland cement–burnt clay and similar puzzolan mixtures may explain the high resistance to sulfate action of mortars made from such materials. As Lea [14] has pointed out, this has long been a perplexing question, since it might have been supposed that any increase in the alumina content of the mortar would tend to promote formation of additional calcium sulfoaluminate and bring about increased deterioration.

6. SUMMARY OF HYDROTHERMAL STUDY

It has been shown that the isometric compounds: $3CaO.Al_2O_3.6H_2O$, $3CaO.Fe_2O_3.6H_2O$, $3CaO.Al_2O_3.3SiO_2$ (grossularite), and $3CaO.Fe_2O_3.3SiO_2$ (andradite), form complete solid solutions with each other. Plazolite ($3CaO.Al_2O_3.2SiO_2.2H_2O$) belongs to this series. Various members of the group were synthesized by hydrothermal treatment of glasses of the proper compositions and by the reaction of iron and aluminum chlorides with boiling calcium hydroxide solution.

The principal product of hydration at elevated temperatures and pressures of various glasses representative of compositions of the liquid phase of cement clinker at 1,400° C, appears to belong to this solid-solution series, as does also the principal hydration product of tetracalcium aluminoferrite. Recent investigations reported by Büssem indicate that hydrates of the calcium aluminosilicate series may be formed during the reaction of mixtures of tricalcium silicate and tricalcium aluminate with water.

Attempts to substitute MgO, MnO, BaO, and SrO for CaO in the series, and to replace Al_2O_3 or Fe_2O_3 by Cr_2O_3, were unsuccessful.

III. X-RAY STRUCTURE STUDIES

By Howard F. McMurdie

1. INTRODUCTION AND METHODS

It was considered desirable to confirm the solid solutions encountered in the foregoing work by a study of the changes in atomic structure involved. In most cases, end members of complete solid-solution series have atomic arrangements in the same space group, or at least in closely related ones, and the change in X-ray pattern from that of one end member to another will be gradual. Thus the positions and relative intensities of the lines will change continuously as the composition varies and not in steps.

Also, since the synthesis of garnet has never before been confirmed by X-ray patterns, it was thought desirable to do so in this investigation.

Because the crystalline material produced by the hydrothermal methods used here was mostly very fine grained, powder patterns were used exclusively in this work.

The samples were mounted on fine glass rods in the center of cylindrical cameras having radii of about 5.7 cm, and were rotated during exposure. Cu $K\alpha$ radiation was used. The radii of the cameras were checked by NaCl. The positions of the lines were measured to 0.01 cm, and the intensities were estimated.

2. STRUCTURE OF $3CaO.Al_2O_3.6H_2O$

The indexed interplanar spacings and relative intensities for the lines of $3CaO.Al_2O_3.6H_2O$ are given in table 6. This pattern indicates a cubic structure with the side of the unit cube equal to 12.56 A ± 0.02.

TABLE 6.—*Interplanar spacing and estimated and calculated relative intensities of* $3CaO.Al_2O_3.6H_2O$

[a=12.56 A]

[*VS*=very strong; *VW*=very weak; *M*=medium; *S*=strong; *W*=weak]

1	2	3	4
hkl	*d*	Estimated relative intensities	Calculated relative intensities
211	5.16	*VS*	1,430
220	4.47	*M*	510
321	3.37	*M*	600
400	3.15	*M*	300
420	2.81	*M*	930
332	(a)	----------	39
422	2.56	*VW*	160
431	2.46	*W*	306
521	2.30	*VS*	1,470
440	2.220	*VW*	72
611-532	2.039	*S*	1,145
620	1.992	*VW*	136
541	(a)	----------	48
631	(a)	----------	23
444	1.812	*VW*	166
543	(a)	----------	15
640	1.741	*W*	270
633-552-721	1.711	*W*	340
642	1.680	*M*	745
651-732	1.600	*VW*	186
800	1.571	*W*	230
840	1.405	*W*	----------

[a] Not observed on film.

As mentioned earlier in the paper, this compound crystallizes in various forms, such as cubes, octahedrons, dodecahedrons, and icositetrahedrons. The fact that all these are holohedral forms indicates strongly that this compound is in the cubic holohedric class.

From a study of the plane indices (hkl) in column 1, it is evident that in all cases $h+k+l=2n$. This indicates a body-centered lattice. There are only two space groups in the cubic holohedral class based on a body-centered lattice: O_h^9 and O_h^{10} Space group O_h^{10} also requires the absence of all first-order reflections of hkO (such as 130, 350, etc.). No such reflections are found in these patterns, and therefore it is almost certain that O_h^{10} is the proper space group.

Grossularite was found to be in this space group by Menzer [15]. He also found eight molecules to a unit cube with $a=11.84$ A, and atomic positions as follows:

16 Al in 16 *a* (0 0 0)[16]
24 Ca in 24 *c* (1/4 1/2 0)
24 Si in 24 *d* (1/4 3/8 0)
96 O in 96 *h* (x, y, z)

with $x=0.04$, $y=0.055$, and $z=0.65$.

This structure consists of tetrahedrons with Si atoms at the centers and O atoms at the corners, the tetrahedrons being connected through Ca and Al atoms. In grossularite, since there are four O atoms for each Si atom, no O atoms are shared by two tetrahedrons, each O atom being bonded to one Si and to Ca or Al atoms. The interatomic distances are typical ones for silicate structures. The distance between O atoms in a single tetrahedron equals about 2.8 A. The distances between Al atoms and O atoms are 1.9 A, while the Ca-O distances are 2.4 A.

It may be assumed that the structure of $3CaO.Al_2O_3.6H_2O$ will be similar. The 16 Al and the 24 Ca atoms can be placed in the same special positions as in garnet. The spaces taken by Si will be vacant, and the O and H atoms will be in the two sets of the general *xyz* positions with different parameters. Because of the extremely low reflectivity of H atoms, it is impossible to place them with any degree of accuracy in a structure having as many heavier atoms as this compound contains.

If the same *xyz* values are assumed for this compound as in grossularite, the effect upon interatomic distances is a general increase of every distance proportioned to the increase of the unit cell from 11.84 Å for the garnet to 12.56 A. This is obviously improbable. The Ca-O and Al-O distances would be expected to remain almost unchanged, and the increased cube size would result not from a general increase but from an increase in O-O distance resulting from the removal of the Si atoms at the centers of the tetrahedrons.

Using $x=0.025$, $y=0.05$, and $z=0.64$, the O-O distances are increased from the 2.8 A in garnet to an average of 3.2 A in $3CaO.Al_2O_3.6H_2O$. The Al-O and Ca-O distances remain the same as in grossularite garnet.

These atomic positions were confirmed by calculating the relative intensities resulting from this arrangement and by comparing them with those estimated from the film.

The formula

$$I_{hkl}=JF^2\left(\frac{1+\cos^2 2\theta}{\sin^2\theta\cos\theta}\right)$$

where

I=relative intensity
J=number of cooperating planes in the form
F=structure factor
θ=glancing angle

was used, with James and Brindley's scattering values [16].

The calculated values of I for all planes possible in O_h^{10} with $h^2+k^2+l^2<64$ are given in column 4 of table 6. The values show good agreement with the estimated intensities.

3. THE SERIES $3CaO.(Al, Fe)_2O_3.3SiO_2$-$3CaO.(Al, Fe)_2O_3.6H_2O$.

As reported in an earlier part of this paper, crystalline products, which are between $3CaO.Al_2O_3.6H_2O$ and grossularite ($3CaO.Al_2O_3.3SiO_2$) in composition, have been prepared hydrothermally. Similar compounds, in which part or all of the alumina has been replaced by Fe_2O_3, have also been prepared. All of these compounds are isotropic and have refractive indices intermediate between those of the end numbers.

To confirm the existence of the solid-solution series by X-ray patterns, it is necessary to find that the positions and relative intensities of the lines of the patterns are intermediate between those of the end members involved. First, patterns of natural garnets of high purity were made. The samples of grossularite ($3CaO.Al_2O_3.3SiO_2$) and andradite ($3CaO.Fe_2O_3.3SiO_2$) were obtained from the National Museum, through the courtesy of W. F. Foshag. Tables 7 and 8 give the indexed powder patterns of these compounds. The unit-cube size found for grossularite was 11.84 A and that of andradite equaled 12.02 A. These agree with the published values for these cell sizes [17].

It is seen that the increase in unit-cell size due to the complete replacement in grossularite of $3SiO_2$ by $6H_2O$ equals 12.56 A$-$11.84 A, or 0.72 A. Any compound of intermediate composition must have a unit cube between these limits if it is a member of this isomorphous series. Table 9 gives unit-cell sizes for various prepared compositions. Those containing no Fe_2O_3 (i. e., 1, 12, 13, 14), and having compositions intermediate between those of $3CaO.Al_2O_3.3SiO_2$ and of $3CaO.Al_2O_3.6H_2O$, in all cases show intermediate unit-cube sizes between those of the above compounds as end members of this series.

TABLE 7.—*Interplanar spacings and estimated relative intensities of grossularite*

[a=11.84 ±0.02 A]

[*VS*=very strong; *VW*=very weak; *M*=medium; *S*=strong; *W*=weak]

hkl	*d*	Estimated intensity
220	4.14	*VW*
400	2.98	*S*
420	2.65	*VS*
332	2.51	*W*
422	2.42	*M*
431	2.33	*M*
521	2.165	*M*
440	2.093	*VW*
611-532	1.928	*S*
620	1.871	*VW*
444	1.711	*M*
640	1.645	*S*
642	1.538	*VS*
800	1.486	*M*
752	1.337	*M*
833	1.296	*S*
664	1.264	*W*
851-784	1.252	*VW*

TABLE 8.—*Interplanar spacings of and estimated relative intensities of andradite*

[a=12.02 ±0.02 A]

[*VS*=very strong; *VW*=very weak; *M*=medium; *S*=strong; *W*=weak]

hkl	*d*	Estimated intensity
220	4.24	*W*
400	3.01	*S*
420	2.69	*VS*
332	2.56	*VW*
422	2.454	*S*
431	2.349	*W*
521	2.195	*W*
611-532	1.951	*M*
620	1.893	*W*
444	1.735	*VW*
640	1.665	*M*
642	1.606	*VS*
800	1.506	*W*
840	1.348	*M*
842	1.309	*M*
932-763	1.249	*M*
941-853	1.214	*VW*
10.40-864	1.113	*M*

TABLE 9.—*Unit-cell size of preparations in the garnet-hydrogarnet series*

Sample number	Molar ratio					a±0.02A
	CaO	Al_2O_3	Fe_2O_3	SiO_2	H_2O	
1	3.06	1.00	----------	0.07	5.97	12.56
2	3.07	0.94	0.06	.41	5.31	12.40
3	3.18	.66	.34	.38	5.84	12.53
4	3.15	.50	.50	.46	5.42	12.64
5	2.88	.31	.69	.23	5.52	12.66
7	3.07	----------	1.00	.38	5.24	12.63
8	3.12	----------	1.00	.42	5.34	12.64
9	3.08	----------	1.00	.54	4.97	12.66
10	3.54	----------	1.00	.52	6.01	12.74
12	3.00	1.00	----------	1.00	3.83	12.25
13	3.11	0.94	----------	2.13	2.27	12.04
14	3.00	1.00	----------	2.94	0.59	11.91
15	3.00	0.50	0.50	1.50	2.55	12.25
16	3.00	.50	.50	2.00	2.15	12.18
17	2.93	.51	.49	2.89	0.55	11.96
18	2.97	----------	1.00	1.98	2.10	12.33
19	2.96	----------	1.00	2.94	0.30	12.09

In the case of number 14, with very little H_2O present, the pattern approaches closely that of natural garnet in the relative intensities as well as in cube size.

The change in cell size resulting from the replacement of Al_2O_3 by Fe_2O_3 can be found by comparing the cell sizes of the two natural garnets. The change equals 12.02 A−11.84 A, or 0.18 A.

Because of the similarity of structure, the same difference in cell size exists between $3CaO.Al_2O_3.6H_2O$ and $3CaO.Fe_2O_3.6H_2O$. Thus it is seen that the cell size of the latter will be 12.56 A (the size of $3CaO.Al_2O_3.6H_2O$) plus 0.18 A or 12.74 A. The same cube size for $3CaO.Fe_2O_3.6H_2O$ is arrived at by considering the increase in size found to result from the complete replacement of $3SiO_2$ by $6H_2O$ in these struc-

tures. It was found to be 0.72. Therefore, the cell size of $3CaO.Fe_2O_3.6H_2O$ will equal 12.02 A (the cell size for $3CaO.Fe_2O_3.3SiO_2$) plus 0.72 or 12.74 A.

As has been explained elsewhere in this paper, it is difficult to prepare pure lime ferrite hydrate. It tends to take up silica from the container during preparation and appears to be unstable when silica is not present. One product, (No. 10), had a cell size of 12.74 A. While this sample contained a small amount of silica, it also had an excess of CaO. Possibly the silica was not in the hydrate structure but was combined with the extra CaO. A pattern of this sample is given in table 10. The cell size of $3CaO.Fe_2O_3.6H_2O$ is therefore believed to be near 12.74 A. Eiger [1] reported the cell size to be 12.71 A, stating that silica was present in his product. It is probable, therefore, that the cell size reported by him is smaller than that of the pure hydrate.

TABLE 10.—*Interplanar spacing and estimated relative intensities for* $3CaO.Fe_2O_3.6H_2O$

[a=12.74 ±0.02 A]

[*VS*=very strong; *VW*=very weak; *M*=medium; *S*=strong; *W*=weak]

hkl	*d*	Estimated intensity
211	5.20	*M*
220	4.54	*S*
321	3.40	*W*
400	3.19	*S*
420	2.85	*S*
332	2.72	*VW*
422	2.60	*M*
431	2.50	*VW*
521	2.326	*M*
611-532	2.069	*M*
541	1.988	*W*
631	1.881	*VW*
543	1.801	*VW*
640	1.766	*M*
721-633-532	1.728	*W*
642	1.702	*VS*
732-651	1.615	*VW*
800	1.590	*W*
822-660	1.500	*W*
840	1.425	*M*
842	1.391	*VW*

Table 9 gives unit-cell sizes of various compositions in this series, all being intermediate between the cell sizes of the end members. Figure 7 shows the relation of cell size to composition.

4. OCCURRENCE OF THE SERIES AS NATURAL MINERALS

The only compound in the series, besides the anhydrous garnets, known to occur as a natural mineral is plazolite ($3CaO.Al_2O_3.2SiO_2.2H_2O$) [7]. The crystal structure of this mineral was studied by Pabst [18], who found plazolite to have a unit cube of 12.14 A and to have atomic position in O_h^{10} similar to garnet.

Previously plazolite has been reported only from Crestmore, California. In this laboratory it has been identified in massive hillebrandite from Velardena, Durango, Mexico.

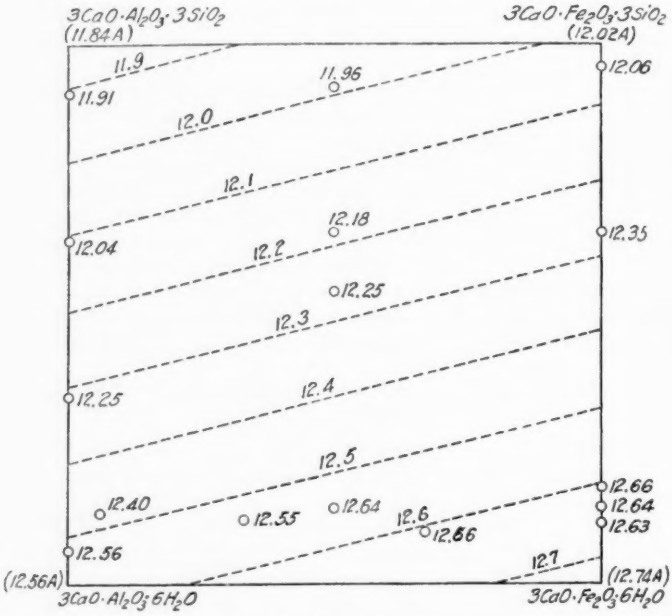

FIGURE 7.—*Variation in unit-cube size with composition in the series* $3CaO.R_2O_3.6H_2O$-$3CaO.R_2O_3.3SiO_2$.

[Mole percent basis]

The hydrothermal production of garnet in this work gives some clue to the method of its formation in rocks. Garnet is not stable at its melting point, since a melt of grossularite composition crystallizes at atmospheric pressure to anorthite, gehlenite, and wollastonite. Garnet largely occurs in metamorphic rocks where there has been great pressure and hydrothermal action may have taken place.

5. SUMMARY OF X-RAY STUDY

An X-ray study has confirmed the existence of an isomorphous series between the four compounds:

$3CaO.Al_2O_3.6H_2O$,
$3CaO.Fe_2O_3.6H_2O$,
$3CaO.Al_2O_3.3SiO_2$, and
$3CaO.Fe_2O_3.3SiO_2$.

These compounds are all cubic and are in the space group O_h^{10}, with eight molecules in the unit cell. The cube size varies from 11.84 A to 12.74 A. In this series, six molecules of H_2O are interchangeable with three molecules of SiO_2. The replacement of SiO_2 by H_2O is accompanied by an increase in cube size of 0.72 A. A replacement of Al_2O_3 by Fe_2O_3 results in an increased cell size of 0.18 A.

The atomic positions in O_h^{10} for $3CaO.Al_2O_3.6H_2O$ are as follows:

16 Al in 16 *a* (0 0 0)
24 Ca in 24 *e* (1/4 1/8 0)
96 O in 96 *h* (x, y, z),

with $x=0.025$, $y=0.05$, and $z=0.64$.

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HYDROLYSIS OF TURANOSE IN ALKALINE SOLUTION [1]

By Horace S. Isbell

ABSTRACT

Turanose (3-α-*d*-glucopyranosido-*d*-fructose) differs from the more common disaccharides in that the glycosidic union is on the carbon adjacent to the reducing group. The proximity of the reducing group influences the stability of the glycosidic union and causes the disaccharide to be particularly susceptible to alkaline hydrolysis. On treatment with limewater, turanose undergoes hydrolysis rather than a normal Lobry de Bruyn interconversion. In the presence of oxygen, in alkaline solution, the sugar is hydrolyzed in large measure and the resulting glucose and fructose are oxidized to arabonic acid. On the other hand, lactulose (4-β-*d*-galactopyranosido-*d*-fructose) is relatively stable to alkaline hydrolysis, and when treated with oxygen in solution containing potassium hydroxide it yields the salt of a disaccharide acid, presumably 3-β-*d*-galactopyranosido-*d*-arabonic acid. The difference in the behavior of the two sugars illustrates the importance of the location of the glycosidic union in relation to the behavior of the sugars in alkaline solution. The location of the glycosidic union also affects the amount of reduction with alkaline copper reagents. Copper-reducing values by the Munson-Walker method are reported for turanose at several concentrations

CONTENTS

	Page
I. Structure of turanose	35
II. Lobry de Bruyn interconversion reaction	37
III. Alkaline hydrolysis of disaccharides	39
IV. Copper-reducing power of turanose and other disaccharides	42
V. Experimental details	44
1. Preparation of the sugars	44
2. Alkaline hydrolysis of turanose in the presence of nitrogen	45
3. Oxidation of turanose, lactulose, and levulose in alkaline solution	45
VI. References	46

I. STRUCTURE OF TURANOSE

For some time doubt has existed concerning the structure of the disaccharide, turanose, obtained by the partial hydrolysis of the trisaccharide, melezitose. In 1926 Zemplén and Braun [1] [2] prepared hendecamethylmelezitose and showed that on hydrolysis it gives 2,3,4,6-tetramethyl-*d*-glucose and a sirupy trimethyl-*d*-fructose which Zemplén and Braun concluded was 1,3,4-trimethyl-*d*-fructose. The separation of 2,3,4,6-tetramethyl-*d*-glucose and 1,3,4-trimethyl-*d*-fructose required that turanose be either a 5-*d*-glucopy-

[1] This paper was presented before the Division of Sugar Chemistry and Technology of the American Chemical Society at Detroit, Mich., September 1940.

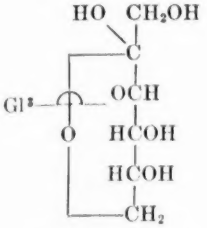
[2] Figures in brackets indicate the literature references at the end of this paper.

ranosido-*d*-fructose or a 6-*d*-glucopyranosido-*d*-fructose. Previously Bridel and Aagaard [2] had shown that the glucosidic group has the alpha configuration. In 1931 Pacsu [3] prepared a tri-triphenylmethyl derivative of turanose which he considered as evidence of the presence of three primary hydroxyl groups. From the work of Zemplén and Braun in conjunction with his tri-triphenylmethyl derivative, Pacsu concluded that turanose is 5-*α*-*d*-glucopyranosido-*d*-fructose. Subsequently Pacsu [4] reported the preparation of four octaacetates of turanose. The existence of four crystalline acetates of turanose could not be explained if the 5-*α*-*d*-glucopyranosido-*d*-fructose structure were correct, unless the assumption were made that some of the acetates were other than the open-chain and pyranoid types. At that time Pacsu concluded that two of the acetates comprise a pair of diastereoisomeric orthoester derivatives of turanose acetate, and that an orthoester structure accounted for the existence of the four acetates. In 1937 Cramer and Pacsu [5] reported a fifth octaacetate and noted the similarity of the supposed orthoester derivatives of turanose to the normal *d*-fructose acetates. In light of this similarity and a difference in the properties of crystalline 1,3,4-trimethyl-*d*-fructose [6] from the properties of the sirupy trimethyl-*d*-fructose of Zemplén and Braun, Pacsu and Cramer [7] stated that the structure of turanose should be reinvestigated. In this connection, it is of interest to note that they apparently did not propose a new structure or state definitely that they had abandoned the 5-*α*-*d*-glucopyranosido-*d*-fructose structure.

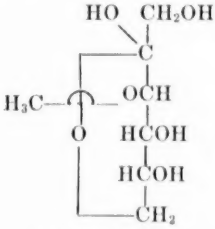
In 1938 Isbell and Pigman [8] showed that the mutarotation reaction of levulose consists of a pyranose-furanose interconversion. They also showed that the changes in optical rotation which take place when turanose is dissolved in water are strictly analogous to those which take place when levulose is dissolved in water. It was therefore obvious that crystalline turanose contains the same modification of the sugar as crystalline levulose. Since the existence of a furanose modification of turanose was not compatible with the 5-*α*-*d*-glucopyranosido-*d*-fructose structure, the subject was discussed and an argument was advanced to show that the glucosidic union of turanose is at carbon 3.

The Isbell and Pigman argument consisted in the following points: (1) The glucosidic group is not attached to carbons 5 or 6 because the sugar is capable of existing in a furanose and a pyranose modification. (2) Turanose forms a disaccharide phenylosazone, and hence the hydroxyl on the first carbon of the *d*-fructose constitutent is free. (3) The phenylosazone of turanose is different from the phenylosazones of maltose and cellobiose (4-*d*-glucopyranosido-*d*-glucosazones), and therefore the glucosidic group is not attached to carbon 4. These points limited the position of the glucosidic group to carbon 3, and inasmuch as there was no reason to doubt the validity of the alpha con-

figuration and the pyranoid ring of the glucosidic group, Isbell and Pigman proposed the structure represented by formula I.



I. 3-α-*d*-glucosido-*d*-fructose (turanose).



II. 3-Methyl-*d*-fructose.

III. 1-Methyl-*d*-fructose.

The argument for the 3-α-*d*-glucopyranosido-*d*-fructose structure depends on the validity of the postulate that a 1-*d*-glucopyranosido-*d*-fructose would not form a disaccharide osazone, whereas a 3-*d*-glucopyranosido-*d*-fructose would. Previous to the Isbell and Pigman publication, Ohle [9] had found that 1-methyl-*d*-fructose (formula III) does not give a 1-methyl-*d*-fructose osazone, whereas Freudenberg and Hixon [10] had found that 3-methyl-*d*-fructose (formula II) does. All precognition supported the postulate that substitution on carbon 1 inhibits osazone formation, but that substitution on carbon 3 does not inhibit osazone formation. Furthermore, Helferich and Bredereck [11] had reported that the sugar obtained by the deacetylation of octaacetyl-1-β-*d*-glucosido-*d*-fructose, when heated with phenylhydrazine, gives a very small quantity of *d*-glucosazone. Helferich and Bredereck did not obtain a disaccharide osazone even though their experimental conditions were like those used for the preparation of turanose osazone. Later Pacsu, Wilson, and Graf [12] reinvestigated the reaction of 1-β-*d*-glucopyranosido-*d*-fructose with phenylhydrazine, and in agreement with the result of Helferich and Bredereck, found that on prolonged heating 1-β-*d*-glucosido-*d*-fructose forms a small quantity of *d*-glucosazone. Pacsu, Wilson, and Graf applied essentially the same argument as that originated by Isbell and Pigman and likewise arrived at the 3-α-*d*-glucosido-*d*-fructose structure.

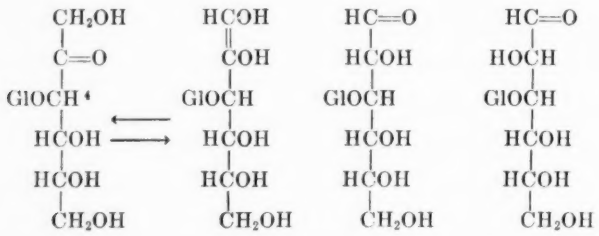
By inspection of formula I it will be observed that the glycosidic group in turanose is attached to the carbon adjacent to the carbonyl group. Since turanose is the only naturally occurring disaccharide in which this relationship is found, it seemed desirable to compare the reactions of turanose with those of other disaccharides.

II. LOBRY DE BRUYN INTERCONVERSION REACTION

As shown by the classical work of Lobry de Bruyn and van Ekenstein [13] and Nef [14], when *d*-fructose is treated with alkali it is converted in part to glucose and mannose. One might anticipate that the aldehydo form of turanose would yield, according to the following

[3] Gl is used to represent the α-*d*-glucosido group.

diagram, 3-α-*d*-glucosido-*d*-glucose (formula VI) and 3-α-*d*-glucosido-*d*-mannose (formula VII). However, when turanose was treated

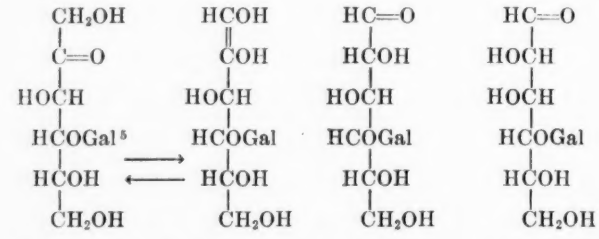


IV. *Aldehydo*-turanose (3-α-*d*-glucosido-*d*-fructose)

V. Turanose 1,2-enediol

VI. *Aldehydo*-3-α-*d*-glucosido-*d*-glucose

VII. *Aldehydo*-3-α-*d*-glucosido-*d*-mannose



VIII. Lactulose

IX. Lactulose 1,2-enediol

X. Lactose (aldehydo modification)

XI. *Aldehydo*-4-β-*d*-galactosido-*d*-mannose

with calcium hydroxide at 35° C, under the conditions which Wolfrom and Lewis [15] found to be most favorable for the interconversion of tetramethyl ethers of *d*-glucose, *d*-mannose, and *d*-fructose, the solution turned dark and it was not possible to isolate a crystalline product. Since there was evidence of decomposition, the reaction of the sugar with lime water was investigated at a lower temperature. At 20° C the solution of turanose remained clear for several days, and it was possible to observe the change in optical rotation. For comparison, measurements were made also with lactulose (4-β-*d*-galactosido-*d*-fructose) (formula VIII). The changes in optical rotation observed for the two sugars are represented by the curves given in figure 1. The increase in dextrorotation displayed by the lactulose solution is in accord with a normal Lobry de Bruyn interconversion; the reaction is merely the reverse of that used for the preparation of lactulose from lactose [16]. The results obtained with the turanose solution, however, cannot be explained by a Lobry de Bruyn interconversion, because the 3-α-*d*-glucosido-*d*-mannose and the 3-α-*d*-glucosido-*d*-glucose which would be formed are more dextrorotatory than turanose and would require an increase in dextrorotation rather than the observed decrease. The decrease requires the formation of a levorotatory substance or the elimination of a strongly dextrorotatory group. If the disaccharide were hydrolyzed the dextrorotatory

[4] Gl is used to represent the α-*d*-glucosido group.
[5] Gal is used to represent the β-*d*-galactosido group.

α-*d*-glucosido group would be eliminated and an equimolecular mixture of *d*-glucose and *d*-fructose would result. This would account for the change in optical rotation and is in harmony with other work relating to the stability of certain disaccharides in alkaline solution.

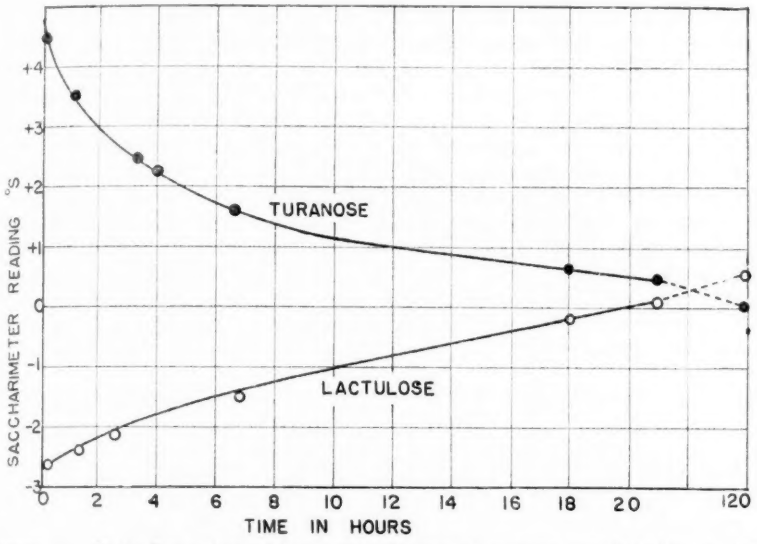
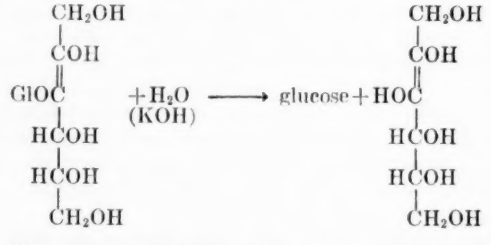


FIGURE 1.—*Optical rotations of 1-percent solutions of turanose and lactulose in 0.04 N calcium hydroxide at 20° C.*

III. ALKALINE HYDROLYSIS OF DISACCHARIDES

From an extensive investigation of the sugars in alkaline solution, Evans and coworkers [17, 18] came to the conclusion that "it is possible for alkaline hydrolysis of *oligosaccharides* to occur in molecules where the biosidic link exists either in the form $\overset{\text{Gl-O-C=}}{|}$, or where the structure can be transformed by the alkaline medium to assume that arrangement." The 2,3-enediol of turanose (formula XII) would contain the $\overset{\text{Gl-O-C=}}{|}$ group, and according to the theory of Evans and coworkers, it should be susceptible to alkaline hydrolysis. Further evidence for the alkaline hydrolysis of turanose was obtained from a study of the sugar in the presence of potassium hydroxide.



XII. Turanose 2,3-enediol. XIII. Fructose 2,3-enediol.

When a solution of turanose in 1 *N* potassium hydroxide was allowed to stand in the absence of oxygen, the solution turned brown, and the optical rotation decreased to zero and finally became levorotatory (table 1). These observations are explained satisfactorily by the rupture of the disaccharide union. The *d*-glucose and *d*-fructose thus formed become enolized and decompose further to give saccharinic acids and dark-colored products. Measurement of the amount of free alkali in the solution at various times shows that acidic substances (presumably saccharinic acids) are formed in considerable quantity. As the reaction proceeds the reducing power of the sugar solution increases to a maximum and then decreases. Inasmuch as the reducing power of the *d*-glucose and *d*-fructose equivalent to a given weight of turanose is 1.88 times that of the disaccharide, the initial increase in reducing power is explained by the alkaline hydrolysis. The subsequent decrease in reducing power may be attributed to the formation of saccharinic acids which have little or no reducing power. Thus the changes in reducing power as well as the changes in optical rotation may be explained by the hydrolysis of the sugar.

TABLE 1.—*Alkaline hydrolysis of turanose by 1 N potassium hydroxide at 25° C in the presence of nitrogen*

Time	Saccharimeter reading [1]	Moles of acid formed per mole of sugar	Relative copper-reducing power [2]
Minutes	° *S*		
2	+15.41	0	1.000
30	+10.73	.11	1.054
77	+6.53	.25	1.077
150	+3.30	.35	1.080
300	+1.43	.42	1.060
715	+0.99	----------	1.007
1,040	−1.01	.51	0.934

[1] Samples of the solution were diluted and acidified before the saccharimeter readings were made.
[2] Based on the copper-reducing power of the first sample as unity.

Additional experiments, however, were devised to confirm the existence of the hydrolytic reaction. The work of Nef [14] and others [19, 20] has shown that the oxidation of reducing sugars in alkaline solution yields products which throw light on the molecular changes. Presumably turanose in alkaline solution gives 1–2 and 2–3 enediols. According to the theory of Nef, the 1–2 enediol would give on oxidation formic and 2-*d*-glucosido-*d*-arabonic acids, while according to the ideas of Evans and coworkers the 2–3 enediol would undergo hydrolysis readily and give a molecule of *d*-glucose and one of *d*-fructose. Spengler, Pfannenstiel, and Nordström [21] have shown that potassium *d*-arabonate can be prepared in good yield by the oxidation of either *d*-glucose or *d*-fructose with oxygen gas in alkaline solution. Hence, if the disaccharide in alkaline solution should be hydrolyzed to *d*-glucose and *d*-fructose, these would be oxidized to potassium *d*-arabonate; but if the sugar were oxidized without hydrolysis, potassium *d*-glucosido-*d*-arabonate would result.

Oxidation experiments with levulose, lactulose, and turanose in alkaline solution showed marked differences. Equimolecular quantities (0.17 mole) of levulose and of turanose gave 2.9 and 1.8 g, respec-

tively, of crystalline potassium *d*-arabonate, while lactulose did not yield any crystalline potassium *d*-arabonate. The separation of potassium *d*-arabonate after the alkaline oxidation of turanose shows conclusively that under the conditions of the experiment the disaccharide union is broken, at least in part. The changes in optical rotation, copper-reducing power, and acidity in the course of the oxidations of turanose levulose and lactulose, by oxygen are given in table 2.

TABLE 2.—*Oxidation of sugars by oxygen in alkaline solution at 25° C.*

Time	Saccharimeter reading [1]	Moles of acid formed per mole of sugar	Copper reducing power of the solution
TURANOSE (3-α-*d*-glucosido-*d*-fructose)			
Minutes	° *S*		
3	+15.31	0	1.000
30	+10.81	0.12	1.061
120	+5.15	.44	1.031
150	+4.73	.51	1.025
225	+3.32	.66	0.952
300	+2.84	.78	.877
375	+2.48	.85	.800
515	+2.29	1.00	.635
1,230	+0.98	1.22	.484
LEVULOSE (*d*-fructose)			
2	−9.73	0	1.000
30	−8.42	0.12	0.891
75	−6.50	.34	.669
150	−4.20	.44	.584
220	−2.38	.68	.418
300	−1.15	.83	.293
516	+0.42	.97	.150
1,320	+.46	1.02	.125
LACTULOSE (4-β-*d*-galactosido-*d*-fructose)			
3	−10.64	--------	1.000
30	−9.14	0.07	0.977
75	−7.24	.16	.926
150	−4.64	.32	.830
225	−2.49	.45	.762
300	−1.01	.57	.700
575	+1.80	.69	.585
810	+2.83	.88	.488
1,350	+3.43	1.09	.396

[1] Samples of the solution were acidified and diluted to a definite volume before the saccharimeter readings were made.

The copper-reducing powers of the levulose and lactulose solutions decrease from the beginning of the experiment, whereas the copper-reducing power of the turanose solution increases to a maximum and then decreases. The increase in reducing power observed for turanose is similar to that found in the absence of oxygen and presumably arises from the hydrolysis of the disaccharide. The optical rotations of the levulose and lactulose solutions change in the direction that would be anticipated for the change accompanying the conversion of levulose to potassium arabonate and of lactulose to potassium 3-*d*-galactosido-*d*-arabonate. The optical rotation of the turanose solution changes in the opposite direction and may be explained satisfactorily by the rup-

ture of the disaccharide union and the subsequent oxidation of the liberated glucose and fructose.

Before considering the reactions of turanose further, it is of interest to note the behavior of melezitose in alkaline solution in the presence of oxygen. Melezitose differs from turanose in that the reducing group in the fructose constituent is blocked by combination with a glucosidic group, and hence it cannot form an enediol. When a sample of melezitose was dissolved in aqueous potassium hydroxide at 20° C in the presence of oxygen, the optical rotation did not change in the course of three days, and after this time nearly all of the melezitose was recovered unchanged. The stability of melezitose under conditions which lead to the cleavage of turanose is further evidence that the sensitivity of turanose to alkaline hydrolysis is related to the presence of a free reducing group in the vicinity of the glycosidic union. It seems probable that similar glycosidic linkages in other naturally occurring products will prove relatively stable to alkaline hydrolysis as long as the carbonyl group is not free. Partially hydrolyzed substances containing free reducing groups in the vicinity of the glycosidic unions, however, will prove susceptible to alkaline hydrolysis.

IV. COPPER-REDUCING POWER OF TURANOSE AND OTHER DISACCHARIDES

A comparison of the reducing powers of turanose with those of other sugars provides information concerning the behavior of the disaccharides in alkaline solution. Previously Isbell, Pigman, and Frush [22] determined the reducing powers of 32 sugars, using a modified Scales method and a copper-citrate reagent buffered with sodium carbonate. Turanose was found to have the lowest reducing power.

It will be noted from the values given in table 3 that the relative molecular reducing powers of the 4-hexosidohexoses and 6-hexosidohexoses are about 1.4 and 1.2, respectively, while the molecular reducing power of turanose is only 0.8. This low reducing power must arise from the unusual structure of turanose. The oxidation of a disaccharide by an alkaline copper reagent can be considered to involve (1) the oxidation and degradation of the reducing portion of the molecule, and (2) the hydrolysis of the disaccharide union and the subsequent oxidation of the fragments set free by hydrolysis. The oxidation and degradation of the reducing portion of the molecule are restricted by the position of the disaccharide union. Without hydrolysis of the disaccharide union, a 3-glucosidofructose, such as turanose, might yield formaldehyde and 2-glucosidoarabinose; whereas, a 4-glucosidofructose might yield formaldehyde, glycol aldehyde, and 2-glucosidoerythrose. Because of the blocking action of the glycosidic group on carbon 3, turanose would give fewer reducing fragments without hydrolysis than any of the other disaccharides listed in table 3. For this reason it might be expected to give the lowest reducing power with reagents which do not cause extensive hydrolysis. The reagents ordinarily used for the determination of reducing sugars, however, are strongly alkaline and, from the behavior of the sugar in aqueous potassium hydroxide one might anticipate considerable hydrolysis. If turanose were hydrolyzed completely before oxidation, the molecular reducing value should approximate that of one molecule of glucose and one molecule of fructose, namely

2,1. The low reducing power (0.8), which was found experimentally, clearly shows that, under the conditions used, the sugar is not completely or even largely hydrolyzed prior to oxidation. Supposedly oxidation and hydrolytic reactions take place simultaneously. At low temperatures in the absence of a vigorous oxidizing agent, the hydrolytic reaction predominates. But at boiling temperatures in the presence of a copper reagent, the sugar is oxidized in large measure without hydrolysis, and the product does not appear to be hydrolyzed and degraded further. In other words, the low reducing power of turanose seems to arise from the formation of some product which is relatively inert in respect to the alkaline copper reagent. This product may be 2-glucosidoarabonic acid which would arise from turanose 1,2-enediol (formula V). The 2,3-enediol (formula XII) would be susceptible to alkaline hydrolysis. Since the relative molecular reducing powers of the 4- and 6-hexosidohexoses listed in table 3 are greater than 1, the glycosidic portion of these disaccharides must contribute to the reducing power, and some hydrolysis must take place. Cleavage of the disaccharide may require that the reducing part of the molecule be first degraded to an intermediate substance which can give the $\mathrm{Gl\,O\text{-}\overset{|}{C}=}$ group that Evans and coworkers [18] have shown to be susceptible to alkaline hydrolysis. In substances containing this group, degradation and hydrolytic reactions may take place simultaneously. Probably the low reducing power of turanose is caused by the lack of the extensive degradation reactions and not by a lack of hydrolysis. The comparatively low reducing power of the 6-hexosidohexoses, on the other hand, may be explained by a lack of sensitivity to alkaline hydrolysis. This lack of sensitivity to alkaline hydrolysis may be due to the location of the glycosidic union at a point which is unfavorable for the formation of a $\mathrm{Gl\text{-}O\text{-}\overset{|}{C}=}$ group.

Measurements of the reducing power of turanose under different conditions gave results which varied considerably and showed that the amount of reduction depends in large measure on the method employed. The relative reducing power of turanose on a weight basis by the Munson-Walker method [23] (table 4) varies with concentration from about 0.53 to 0.56; by a modified Scales method [22] the relative reducing power is only 0.41. Presumably the higher value obtained with the Munson-Walker method is due to more hydrolysis, caused by the higher alkalinity of the reagent.

It was mentioned, in connection with the interpretation of the analytical data for the alkaline hydrolysis of turanose, that when a turanose solution is treated with alkali the copper-reducing power increases, and that this increase in reducing power is caused by the hydrolysis of the sugar. Since on hydrolysis one molecule of turanose yields one molecule of glucose and one molecule of fructose, the reducing power of hydrolyzed turanose is equal to that of a corrresponding quantity of invert sugar. A calculation from the Munson-Walker values [23, 24] for the reducing power of invert sugar shows that the quantity of invert sugar which would be obtained by the hydrolysis of 0.1 g of turanose would yield 0.2274 g of cuprous oxide. This is 1.88 times the quantity of cuprous oxide produced by 0.1 g of turanose.

TABLE 3.—*Relative reducing powers of disaccharides* [1]

Sugar	Relative reducing power. Glucose=1	
	Molecular basis [2]	Weight basis
4-β-*d*-Glucosido-*d*-mannose	1.49	0.78
4-β-*d*-Glucosido-*d*-glucose (cellobiose)	1.47	.77
4-α-*d*-Glucosido-*d*-glucose (maltose)	1.39	.73
4-β-*d*-Galactosido-*d*-glucose (lactose)	1.42	.75
4-β-*d*-Galactosido-*d*-fructose (lactulose)	1.39	.73
4-β-*d*-Galactosido-*d*-altrose (neolactose)	1.44	.76
6-β-*d*-Glucosido-*d*-glucose (gentiobiose)	1.20	.63
6-α-*d*-Galactosido-*d*-glucose (melibiose)	1.18	.62
3-α-*d*-Glucosido-*d*-fructose (turanose)	0.77	.40

[1] Values determined by Isbell, Pigman, and Frush [22] with an alkaline copper-citrate reagent.
[2] The ratio of the reduction produced by the quantity of the sugar, molecularly equivalent to 15 mg of *d*-glucose, to that produced by 15 mg of *d*-glucose.

TABLE 4.—*Comparative reducing power of turanose and glucose (Munson-Walker method)*

Turanose	Milligrams of cuprous oxide produced by sample	Glucose [1] equivalent to same quantity of cuprous oxide	Relative reducing ratio.[2] Glucose=1 (weight basis)
Mg			
100	121.1	52.9	0.529
200	239.4	107.9	.539
250	299.8	137.3	.549
350	414.5	195.7	.559

[1] Data from the work of Hammond [24].
[2] The "relative reducing ratio" is the ratio of the weight of dextrose to the weight of turanose required to give like reduction.

V. EXPERIMENTAL DETAILS

1. PREPARATION OF THE SUGARS

Melezitose.—The melezitose was prepared in 1928 in collaboration with C. S. Hudson from some melezitose honey [25] kindly supplied by the Office of Bee Culture Investigations, United States Department of Agriculture. From 250 kg of melezitose honey 13 kg of pure melezitose was obtained. A part of the material was recrystallized and used in this investigation. In a 4-percent aqueous solution it gave $[\alpha]_D^{20}=+88.2$.

Turanose.—The turanose was prepared by the method of Hudson and Pacsu [26]. Crystallization was induced by seed crystals kindly supplied by D. H. Brauns, who was the first [26, p. 2521] to discover and separate crystalline turanose. The sugar was recrystallized by concentrating an aqueous solution containing 100 g of turanose to a sirup ($n_D^{20}=1.490$) which was dissolved in 100 ml of hot methyl alcohol. The clear alcoholic solution was allowed to cool, after which it was seeded and kept for several days while crystallization took place. In a 4-percent aqueous solution, the resulting crystals gave $[\alpha]_D^{20}=+27.3$ initially, changing in the course of an hour to an equilibrium value of $+75.8$.

Lactulose.—The lactulose was prepared by the method of Montgomery and Hudson [16] without the use of seed crystals. The product was recrystallized by essentially the same procedure as that used for turanose. In 4-percent aqueous solution the material gave $[\alpha]_D^{20} = -11.9$ initially, changing in several hours to -50.7.

2. ALKALINE HYDROLYSIS OF TURANOSE IN THE PRESENCE OF NITROGEN

A sample of pure crystalline turanose (5.7 g) was dissolved in 50 ml of 1 *N* potassium hydroxide solution, with stirring, while a small stream of nitrogen was bubbled through the solution, which was kept at 25° C. From time to time, 5-ml samples of the alkaline solution were taken and mixed quickly with 10 ml of 0.5 *N* hydrochloric acid. Time was measured for each sample, beginning with the dissolution of the sugar and ending with the addition of the hydrochloric acid. The optical rotation of the acidified solution was read with a Bates saccharimeter in a 2-dm tube at 20° C. A 10-ml portion of the solution used for the optical rotation measurement, was transferred to a 50-ml graduated flask and titrated with 0.2 *N* potassium hydroxide, using phenolphthalein as an indicator. The volume of the original sugar solution was 54 ml and the sample for each titration corresponded to 3.33 ml of the original sugar solution, or 0.00103 mole of sugar. After the titrations were completed, the solutions were diluted to 50 ml and reducing-sugar determinations were made by the Munson-Walker method. The weights of cuprous oxide obtained from 20 ml of the diluted solution were divided by the weight of the cuprous oxide obtained from the sample taken at the beginning of the experiment to give the "relative copper-reducing power." The results are given in table 1.

3. OXIDATION OF TURANOSE, LACTULOSE, AND LEVULOSE IN ALKALINE SOLUTION

The oxidation experiments were conducted essentially like the alkaline hydrolysis described in the preceding section, except that oxygen gas was used in place of nitrogen and larger quantities were employed in order to provide material for the isolation of the product. In these measurements, 0.033 mole of the sugar was dissolved in 100 ml of 1 *N* potassium hydroxide, and the solution was kept saturated with oxygen. The optical rotations, moles of acid formed per mole of sugar, and the copper-reducing values were measured in the same manner as in the experiments in the presence of nitrogen. The methods are described in the preceding section, and the results are recorded in table 2.

After the oxidation experiment had proceeded for 22 hours, the reaction was stopped by saturating the alkaline solution with carbon dioxide. To isolate the product, 50 ml of the solution was concentrated to a sirup, which was diluted with alcohol and seeded with crystalline potassium arabonate. The sample from the levulose experiment gave 2.9 g of crystalline potassium arabonate, while that from the turanose experiment gave 1.8 g. The experiment with lactulose did not yield any crystalline potassium arabonate even though a careful search was made. The product in the evaporated

solution from the lactulose experiment was precipitated by the addition of ethyl alcohol as a light-colored sirup which has failed to crystallize. Before hydrolysis, the sirupy product did not reduce Fehling's solution. After boiling for a few minutes with aqueous hydrochloric acid, the hydrolyzed product gave a strong test for reducing sugar. These observations may be explained by the presence of a bionic acid, presumably 3-β-*d*-galactosido-*d*-arabonic acid.

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RESEARCH PAPER RP1357

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PREPARATION OF *d*-MANNOSE

By Horace S. Isbell

ABSTRACT

An improved method for the preparation of *d*-mannose from ivory-nut shavings is reported. This method differs from previous ones in that the sugar is crystallized from a mixture of methyl and isopropyl alcohols. The yield of crystalline sugar, based on the weight of ivory-nut shavings, is approximately 35 percent.

Although several investigators [1, 2, 3, 4, 5, 6, 7] [1] have given directions for the preparation of *d*-mannose from ivory-nut turnings, obtained from button factories, the methods are not entirely satisfactory. Various workers have prepared large quantities of mannose by the method of Hudson and Sawyer [3]; but, as pointed out by Hudson and Jackson [7], the results have not been consistently good. Hudson and Jackson sought to improve the method by first preparing pure crystalline α-methyl *d*-mannoside from vegetable ivory and then converting the pure glycoside to *d*-mannose. The process, although successful, requires two hydrolyses and considerable labor. At various times during the past 10 years the writer has had occasion to prepare crystalline *d*-mannose and has made certain improvements in the method. With these improvements it is possible to obtain consistently good results in the preparation of the sugar without the intermediate preparation of the methyl glycoside or other derivative. The method used is similar to that described by Clark [4] but differs in that the sugar solution is purified by precipitation of impurities with a mixture of methyl and isopropyl alcohol.

Method.—One kilogram of screened ivory-nut shavings [2] is mixed with 1 kg of cold 75-percent sulfuric acid (430 ml of concentrated sulfuric acid and 250 ml of water). The material is triturated until the sulfuric acid is uniformly distributed, and allowed to stand until the next day, preferably at about 35° C. The mass is then dissolved in 10 liters of water, and the solution is filtered through cheesecloth. The filtrate is heated to boiling for 6 hours while the volume is maintained approximately constant. The hot liquid is then neutralized with barium carbonate, using a commercial antifoam agent or capryl alcohol to reduce foaming. After the addition of 200 g of a decolorizing carbon, the barium sulfate is allowed to settle and is separated by filtration. The filtrate is evaporated in vacuo to a sirup of about 85-percent total solids ($n_D^{20}=1.503$). This sirup is thoroughly mixed with 1 liter of warm methyl alcohol, after which

[1] Figures in brackets indicate the literature references at the end of this paper.

[2] The ivory-nut shavings may be purchased from the Button Machinery Co., 11th, Grand, and Adams Street, Hoboken, N. J.

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the solution is diluted with 2 liters of isopropyl alcohol.[3] This results in the precipitation of some gummy amorphous material, which is separated by decantation. The larger part of the mannose is in the alcoholic extract; that in the gummy residue is separated by triturating the gum with 250 ml of methyl alcohol and then adding 500 ml of isopropyl alcohol. The mixture is allowed to settle, and the insoluble residue is separated from the alcoholic extract. The residue thus obtained is given a second treatment with methyl and isopropyl alcohols, and the alcoholic extracts are combined. After the addition of about 50 g of a decolorizing carbon, the solution is filtered and evaporated in vacuo. Crystalline α-*d*-mannose usually separates as the solution becomes concentrated. The evaporation is continued until a massecuite is obtained, whereupon evaporation is stopped and the crystals are separated. If crystallization does not occur spontaneously, the thick sirup is diluted with 200 ml of methyl alcohol and seeded with α-*d*-mannose. About 250 g of crystalline mannose separates in the first crop and approximately 100 g additional may be obtained by evaporating the mother liquors to a thick sirup containing about 85-percent total solids. The thick sirup is taken up in methyl alcohol and brought to crystallization by seeding with α-*d*-mannose.

Recrystallization.—One hundred grams of crude mannose is dissolved in 100 ml of water. After the addition of a few drops of acetic acid and 5 g of a decolorizing carbon, the solution is filtered and evaporated in vacuo to a heavy sirup ($n_D^{20}=1.511$). The sirup is mixed with 50 ml of warm methyl alcohol, followed by 200 ml of a mixture containing equal volumes of methyl and isopropyl alcohols. The sirup is decanted from any gummy material, filtered, if necessary, and then seeded with about 0.5 g of α-*d*-mannose and allowed to crystallize, preferably while kept in motion. In the course of 1 or more days, about 75 g of the crystalline sugar separates. By concentrating the mother liquor and repeating the process, nearly all of the mannose can be separated in the crystalline state.

In 4-percent aqueous solution α-*d*-mannose gives $[\alpha]_D^{20}=+29.3$ initially, changing in the course of several hours to an equilibrium value of +14.2.

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WASHINGTON, October 25, 1940.

[3] Commerical 99-percent isopropyl alcohol and technical synthetic methyl alcohol are suitable for this preparation.

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EFFECT OF HEAT TREATMENT AND COOLING RATE ON THE MICROSCOPIC STRUCTURE OF PORTLAND CEMENT CLINKER

By George W. Ward

ABSTRACT

Ten commercial portland cement clinkers with their slowly and quickly cooled counterparts were examined microscopically. Methods are given for the conduction of the microscopical examination.

The appearance of the clinker phases after the different heat treatments is described and the structure of the clinkers discussed.

In general, for all clinkers, the phase compositions as calculated with consideration of glass agreed better with the microscopically determined phases than did those based upon the calculations in which complete equilibrium crystallization was assumed. The microscopically determined $3CaO.SiO_2$ was nearly always greater and the $2CaO.SiO_2$ lower than that calculated by either of the other methods. The $3CaO.Al_2O_3$ was always less than that calculated from chemical analyses. Generally the $4CaO.Al_2O_3.Fe_2O_3$ found microscopically exceeded that calculated by either of the other methods. The glass determined microscopically and the values obtained from the heat of solution method agreed better for slowly and plant cooled than for quickly cooled clinkers.

CONTENTS

	Page
I. Introduction	49
1. Heat treatment	50
2. Methods of examination	50
II. Description of clinker minerals	50
1. Free lime	51
2. Magnesia	51
3. Tricalcium silicate	51
4. Dicalcium silicate	52
5. Dark interstitial material	52
6. Tetracalcium aluminoferrite	54
III. Comparison of phase compositions as determined microscopically and as calculated from analytical data	54
IV. Summary	63
V. References	64

I. INTRODUCTION

Investigators have recognized that the relative proportions of the phases in portland cement clinker exert an important influence on the properties of the resulting concrete. In recent years successful attempts have been made to vary the relative proportions of the constituents by changing the cooling rate of clinker [1].[1] Correlations between calculated clinker compositions assuming complete crystallization and the physical properties of the resulting cements have not

[1] Figures in brackets indicate the literature references at the end of this paper.

been precise. Comparisons between calculated and microscopically determined phase compositions of commercial clinkers have been published recently [2].

In the present report data are presented upon variously heat-treated clinkers as well as the plant products. New information was gained on the microscopic structure of portland cement clinker. The effects of heat treatment, particularly the rate of cooling, on the phases present are described. Correlations are made between observed phases and calculated phase compositions.

1. HEAT TREATMENT

Ten samples were taken from a series of 26 commercial clinkers which covered the range of compositions found in commercial practice. One portion of each clinker, designated as *P* or "plant" clinker, was examined in its original condition. A second portion of each clinker was reheated in an experimental rotary kiln (5 in. by 8 ft) at a temperature of 1,400° to 1,425° C (2,552° to 2,597° F) and cooled to 1,250° C (2,282° F) in 2 to 3 minutes in order to yield a maximum amount of glass. This quickly cooled clinker was designated as *Q*. A third portion was reheated to the same temperature in a laboratory batch kiln and cooled to 1,250° C (2,282° F) at a uniform rate in about 3 hours in order to yield a minimum of glass. This slowly cooled clinker was designated as *S*. The heating and cooling were carried out under oxidizing conditions. The 10 random clinkers with their variously heat-treated counterparts gave 30 samples for study.

2. METHODS OF EXAMINATION

The clinkers were studied microscopically and were analyzed chemically.[2] The investigation with the microscope included examination of powders, thin [3] and polished thin sections [4], together with variously etched polished specimens [4, 5, 6].

Quantitative measurements were made using etched, polished specimens suitably mounted in Bakelite resin [6]. When ready for examination the surface of each specimen contained from 15 to 20 clinker particles. All quantitative measurements were made with a Wentworth [7] micrometer attached to the microscope stage. Each value reported was the average of five equally spaced traverses on each of five mounts.

The etchants proposed by Tavasci [4] and Insley [5], with modifications in some instances, were found to be generally satisfactory.

Glass was determined microscopically after a water etch followed by 1-percent nitricacid-alcohol solution, and after an etch by 10-percent potassium hydroxide in water [8].

II. DESCRIPTION OF CLINKER MINERALS

The various clinker phases are described below as they appeared in etched polished specimens when viewed microscopically by reflected light. Figures 1, 2, and 3, although used to illustrate the typical appearance of all clinkers after the various heat treatments, represent

[2] Analyses by C. L. Ford, Portland Cement Association, Chicago, Ill.

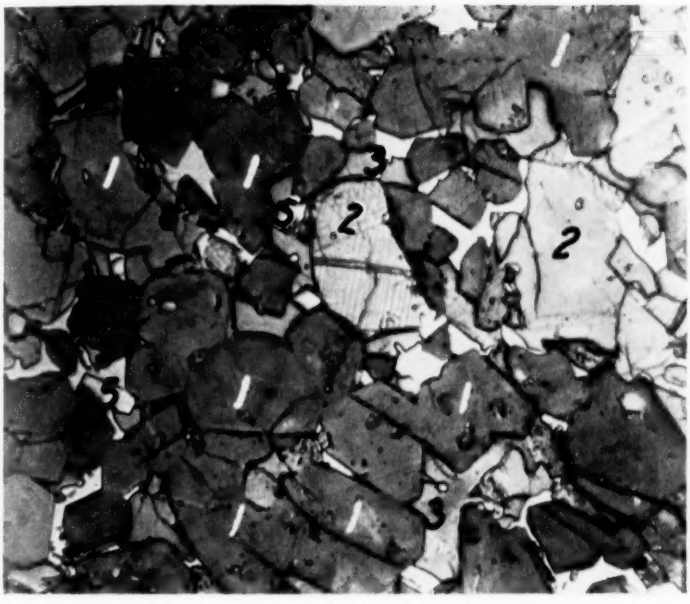

FIGURE 1.—*Typical slowly cooled clinker.*

1, $3CaO.SiO_2$; 2, β—$2CaO.SiO_2$; 3, $3CaO.Al_2O_3$; 4, $4CaO.Al_2O_3.Fe_2O_3$; 5, MgO. Distilled water and nitric acid etch. Magnification ×500. Reflected light.

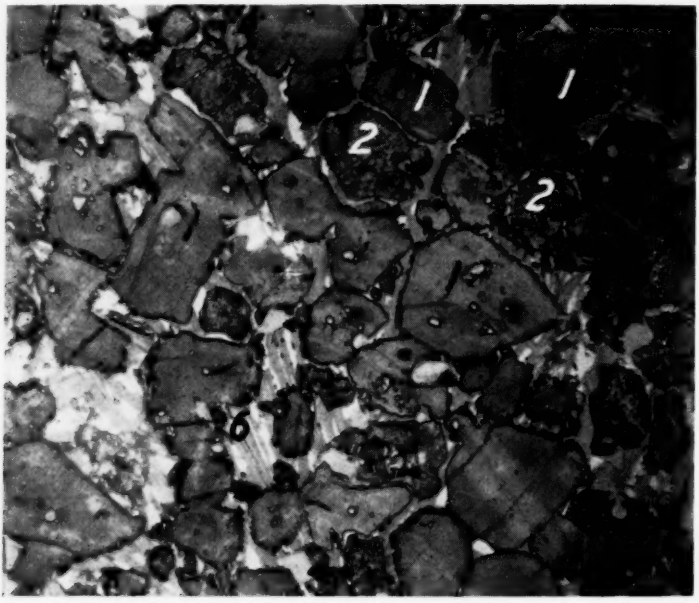

FIGURE 2.—*Typical plant-cooled clinker.*

1, $3CaO.SiO_2$; 2, $\beta-2CaO.SiO_2$; 4, $4CaO.Al_2O_3.Fe_2O_3$; 6, prismatic dark interstitial material, arrows indicate unknown phases. Note $\beta-2CaO.SiO_2$ rims around $3CaO.SiO_2$. Distilled water and nitric acid etch. Magnification ×500. Reflected light.

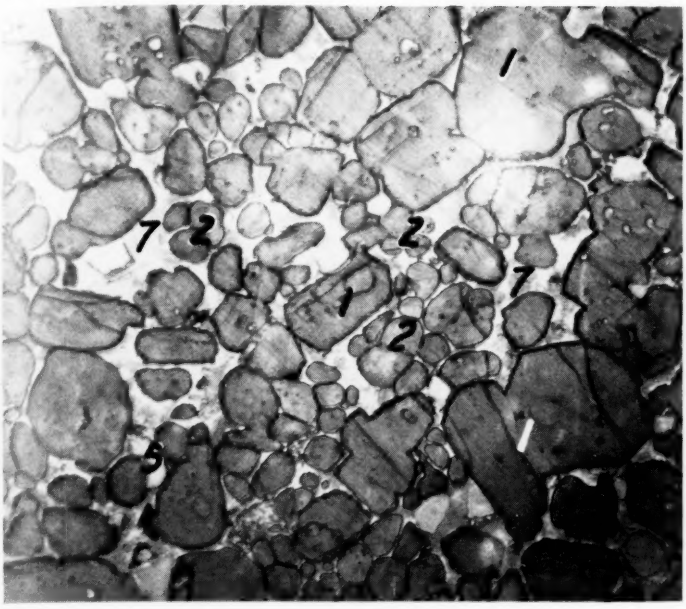

FIGURE 3.—*Typical quickly cooled clinker.*

1, $3CaO.SiO_2$; 2, $\beta-2CaO.SiO_2$; 5, MgO; 7, glass and light interstitial material, $4CaO.Al_2O_3.Fe_2O_3$. Distilled water and nitric acid etch. Magnification ×500. Reflected light.

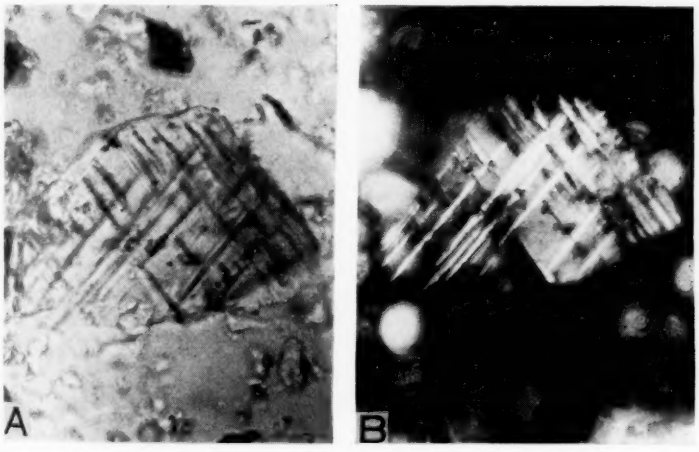

FIGURE 4.—$3CaO.SiO_2$ *in transmitted light, twinning simulated by unknown inclusions.*

A, Uncrossed Nicols; *B*, crossed Nicols. Magnification ×1000. Transmitted light.

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specifically the changes effected in sample 3 by slow, plant, and quick cooling, respectively.

1. FREE LIME

Free lime (CaO) etched readily after 1 minute's exposure in 1–3 water-alcohol. It appeared as dark gray, almost black, rounded, or elliptical grains with no zoning, twinning, or inclusions. It occurred as inclusions in $3CaO.SiO_2$ and in the interstitial material. As the cooling became slower the amount of free lime decreased.

In general, free lime was the first phase to crystallize. However in slowly cooled clinkers, where the cooling occurred at a uniform rate from 1,450° to 1,250° C in about 3 hours, some of the free lime crystallized after $3CaO.SiO_2$.

2. MAGNESIA

Magnesia, or periclase (MgO), was observed without etching as brilliant crystals of high relief occurring well distributed throughout the interstitial material and occasionally in slowly cooled and plant-cooled clinkers, as inclusions in $3CaO.SiO_2$. As the cooling became slower crystal form became more prominent, octahedrons being found in slowly cooled clinker. Cracking around the rims of the grains almost always occurred, but it tended to decrease in quickly cooled clinkers, possibly because of the small crystal size in that type of clinker. By actual measurement of many periclase particles, their average size was found to be greater in slowly cooled than in plant-cooled clinkers, and larger in plant-cooled than in quickly cooled clinkers.

3. TRICALCIUM SILICATE

Tricalcium silicate ($3CaO.SiO_2$) etched as dark gray, almost black, crystals after 3 to 5 seconds agitation in 1-percent HNO_3-alcohol mixture. Probably because of difference in orientation, a few crystals etched to a lighter color. It was commonly the most abundant phase. In slowly cooled clinkers it tended to be completely or partially included in tricalcium aluminate crystals. The development of good crystal form was observed to decrease with increased rate of cooling.

Re-solution [3] of $3CaO.SiO_2$ and the resulting precipitation of $\beta 2CaO.SiO_2$ were more prominent in slowly cooled than in plant-cooled clinkers and only very limited in quickly cooled clinkers. This re-solution was indicated by embayed tricalcium silicate with dicalcium silicate occupying the bays and frequently by fringes of dicalcium silicate around tricalcium silicate. The particularly good examples of partial and complete pseudomorphs of dicalcium silicate after tricalcium silicate in specimens *4P* and *7P* were other indications of re-solution.

The tendency to form twins or to be zoned decreased as the cooling became more rapid. Good examples of simple twinning were found in slowly cooled and plant-cooled clinkers with a greater number in the former. Zoning was well developed in the slowly cooled clinker, with three or four zones not unusual, but it was developed to a lesser extent in the plant-cooled product and was rarely observed in quickly cooled samples.

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[3] L. S. Brown considers this as dissociation; see "Tricalcium Aluminate and the Microstructure of Portland Cement Clinker." Proc. Am. Soc. Testing Materials **37**, pt. 2, 279 (1937).

Inclusions of dicalcium silicate, magnesia, and free lime, sometimes accompanied by tetracalcium aluminoferrite, frequently occurred in tricalcium silicate irrespective of heat treatments. In a few instances periclase inclusions had dark halos, possibly indicative of solution in tricalcium silicate. In clinkers *4P* and *4Q* a special type of inclusion arranged to simulate complex twinning, as seen in dicalcium silicate, was noted. Because of their small size, it has not been possible to identify these inclusions, although they resemble in arrangement and general appearance the crystallization of calcium ferrite from tricalcium silicate found by Anderson and Lee [9] in slag. This phenomenon is illustrated in figure 4.

4. DICALCIUM SILICATE

Dicalcium silicate ($2CaO.SiO_2$). β-Dicalcium silicate appeared without good crystal f m, generally as spherical or elliptical crystals, which etched readily 1-percent nitric-acid–alcohol solution. Their distribution was gen y good, but in some clinkers there was a strong tendency to form large groups. Commonly β-dicalcium silicate occurred closely associated with tricalcium silicate as fringes, as inclusions, as pseudomorphs, or occupying embayments.

In quickly cooled clinkers, dicalcium silicate with complex twinning was the most frequently observed form of this phase. Occasionally free lime was found as inclusions, and tetracalcium aluminoferrite appeared along twinning planes and in cracks. Simplicity of form, a general lack of inclusions, and fewer irregularities characterized the dicalcium silicate of quickly cooled clinkers.

In slowly cooled clinkers, dicalcium silicate untwinned and with simple multiple twinning was more prominent. Frequently twinning extended out past the usually rounded-particle boundary to give a many-fingered appearance to the grain. It was not unusual for twinning to be indicated by an arrangement of small unidentifiable inclusions. Dicalcium silicate was often cracked radially and sometimes completely separated by cracking or embayment. The appearance of dicalcium silicate, in plant-cooled clinker, was characteristic of that found in either slowly or quickly cooled clinkers, since plant cooling was intermediate between these two cooling rates.

γ-Dicalcium silicate, sometimes in considerable amounts, was observed only in slowly cooled clinkers.

5. DARK INTERSTITAL MATERIAL

Dark interstitial material consists of three types: rectangular (identified as $3CaO.Al_2O_3$), dark prismatic interstitial material, and glass.

Tricalcium aluminate ($3CaO.Al_2O_3$) etched readily in freshly distilled water to dark-gray rectangular masses, occasionally showing square outlines, and was often intimately associated with tetracalcium aluminoferrite. Where present it was distributed throughout the

clinker structure and sometimes completely occupied the interstices. Roughly square or rectangular shapes were generally observed, but irregular areas appeared sometimes with the trace of one crystal face. There was no evidence of corrosion, twinning, or zoning. The inclusions were dicalcium silicate, tricalcium silicate, and infrequently periclase. Small, scattered, bubble-like inclusions of what may be tetracalcium aluminoferrite occurred.

Tricalcium aluminate was found in slowly cooled clinkers when the Al_2O_3-Fe_2O_3 ratio was 1.63 or greater, and not in those of Al_2O_3-Fe_2O_3 ratio 0.97 or less. In the group studied, clinkers having Al_2O_3-Fe_2O_3 ratios between 0.97 and 1.63 were not available.

Only two of the plant-cooled clinkers contained tricalcium aluminate. One of these had an Al_2O_3-Fe_2O_3 ratio of 1.89 and a low total alkali content (0.22 percent). The other had an Al_2O_3-Fe_2O_3 ratio of 2.91, the highest in this group, and a total alkali content of 1.00 percent. In this latter case, only a small percentage of the tricalcium aluminate calculated to be present at crystalline equilibrium appeared. In quickly cooled clinkers tricalcium aluminate was not found.

Prismatic dark interstitial material when etched in freshly distilled water appeared as dark-gray, almost black, elongated crystals, frequently with darkened edges. It showed no corrosion, twinning, or zoning. Occasionally the crystals were bordered by ragged, weakly etched dark interstitial material which was identified as glass. Scattered crystals and aggregates appeared throughout the clinker as slender, needle-like, and large, poorly terminated crystals. Frequently they terminated against silicates. In thin sections viewed with transmitted light these crystals were anisotropic with a birefringence of about 0.010 and parallel extinction. Their refractive indices were close to 1.72 [6].

Prismatic dark interstitial material was much more abundant in plant-cooled than in slowly or quickly cooled clinkers. The quantity of this constituent appeared to be influenced by the rate of cooling. The high glass content of quickly cooled clinkers indicated that rapid cooling prevents crystallization of prismatic dark interstitial material, since this compound is one of the last to crystallize. This phase was more frequent in occurrence and better in development for high Al_2O_3-Fe_2O_3 ratio clinkers containing appreciable amounts of Na_2O and K_2O either alone or together.

Glass is revealed by etching with 10 percent KOH [8]. The etchability of glass in other reagents depends on its composition. For instance, glass low in iron is readily etched with water followed by 1 percent HNO_3 in alcohol, and glass high in iron is unaffected by this etchant method [10].

The amount of glass varied greatly with different cooling rates. In slowly cooled clinker it occurred infrequently and was seen edging prismatic dark interstitial material. In plant-cooled clinker it occurred as irregular areas, blebs, small veinlets, and frequently as a

jagged sheath around dark prismatic crystals. Etched, quickly cooled clinkers revealed glass as ragged areas, blebs, and veinlets. Occasionally it had a roughly prismatic form due to prior crystallization of tetracalcium aluminoferrite prisms. When in the form of blebs, it frequently gave the light interstitial material a mottled appearance which made difficult its differentiation from tetracalcium aluminoferrite.

6. TETRACALCIUM ALUMINOFERRITE

Tetracalcium aluminoferrite ($4CaO.Al_2O_3.Fe_2O_3$) was unaffected by most etchants and appeared as light interstitial material intimately associated with dark interstitial material.

In the clinkers investigated, tetracalcium aluminoferrite was the last crystalline phase to appear except in compositions of low Al_2O_3-Fe_2O_3 ratios, where the tricalcium aluminate gave every indication of having been the last phase to crystallize.

In slowly cooled clinkers well-developed prisms of tetracalcium aluminoferrite were easily recognized in thin sections. The prism forms varied with the Al_2O_3-Fe_2O_3 ratio—large, broad forms predominating in clinkers of low ratio and small needle-like forms in those of high ratio. There was very little change from the amber color and slight pleochroism of the pure compound.

In quickly cooled clinkers tetracalcium aluminoferrite appeared as long, narrow prisms irrespective of the Al_2O_3-Fe_2O_3 ratio. It was also frequently found as dentritic growths in clinkers having low Al_2O_3-Fe_2O_3 ratios. The large, broad prisms found in slowly cooled clinker were practically absent. In many cases the amber color of this phase was darker and greener while the pleochroism became more pronounced, which may have been due to solid solution with MgO [11]. Insley and McMurdie [12] pointed out from their studies that there must be less than 1 percent of MgO in solid solution in tetracalcium aluminoferrite.

III. COMPARISON OF PHASE COMPOSITIONS AS DETERMINED MICROSCOPICALLY AND AS CALCULATED FROM ANALYTICAL DATA

The phases in portland cement clinker are usually calculated from chemical analyses without regard to the rate of clinker cooling. In order to show the inaccuracies which develop from this procedure, comparisons of data obtained from microscopical analyses are made with those obtained from chemical analyses by two methods of calculation.

The percentages by weight of the various phases, calculated from microscopical observations and from chemical analyses, are given in table 2, arranged in order of increasing Al_2O_3-Fe_2O_3 ratios for similar

cooling conditions. The columns designated "Micro" contain results of microscopical analyses. It is necessary to assume in calculating data such as these that each phase is pure and that the effects of zoning and solid solution are negligible. In order to convert volume percentages to weight percentages the following density values [2] were used: $3CaO.SiO_2$, 3.13; β-$2CaO.SiO_2$, 3.28; $4CaO.Al_2O_3.Fe_2O_3$, 3.77; CaO, 3.32; MgO, 3.58. Since the composition of the glass is variable and uncertain, a density value of 3.00 [2] was used for all dark interstitial material.

TABLE 1.—*Chemical analyses of clinkers arranged in order of increasing* Al_2O_3/Fe_2O_3 *for similarly cooled clinkers*

[Chemical analyses by C. L. Ford, Research Lab., Portland Cement Assn., Chicago]

No.	Al_2O_3/Fe_2O_3	SiO_2	Fe_2O_3[a]	Al_2O_3[b]	CaO[c]	MgO	Free CaO	SO_3	FeO	TiO_2	Na_2O	K_2O	Ignition Loss	Insoluble Residue
		%	%	%	%	%	%	%	%	%	%	%	%	%
4S	0.65	19.74	7.11	4.61	62.93	4.28	0.30	0.12	0.00	[d]N. D.	0.41	0.10	0.14	0.11
4P	.89	19.84	5.33	4.73	58.51	4.24	4.20	.13	1.46	0.37	.53	.20	.23	.39
4Q	.81	19.51	6.04	4.91	61.24	4.37	1.51	.08	1.27	N. D.	.37	.12	.00	.21
11S	.87	22.24	4.89	4.24	66.54	0.85	0.08	.06	0.00	N. D.	.52	.05	.14	.16
11P	.90	21.98	5.07	4.54	66.17	.81	.16	.11	.00	.34	.66	.16	.18	.20
11Q	.95	22.38	4.32	4.08	66.51	.82	.34	.12	.33	N. D.	.51	.08	.11	.17
2S	.97	21.27	5.12	4.97	64.99	1.72	.06	.45	.05	N. D.	.27	.37	.12	.20
2P	1.01	20.62	5.49	5.54	63.32	1.80	.77	.61	.15	.42	.33	.71	.17	.15
2Q	1.12	20.90	4.88	5.45	63.96	1.85	.85	.18	.63	N. D.	.24	.30	.08	.26
8S	1.63	22.66	2.98	4.86	64.63	3.93	.07	.19	.00	N. D	.15	.25	.17	.18
8P	1.64	22.51	3.02	4.95	63.93	3.53	.61	.25	.00	.35	.17	.49	.25	.14
8Q	1.65	22.79	2.95	4.86	64.37	3.52	.79	.10	.03	N. D.	.10	.08	.19	.23
10S	1.68	23.68	2.88	4.83	65.34	1.30	.18	.28	.00	N. D.	.26	.33	N. D.	N. D.
10P	1.68	23.48	2.86	4.79	62.89	1.29	2.06	.57	.00	.33	.34	.81	.45	.20
10Q	1.68	23.69	2.89	4.84	63.57	1.30	1.96	.22	.00	N. D.	.26	.37	N. D.	N. D.
6S	1.88	21.85	3.08	5.81	67.02	1.43	0.00	.12	.00	N. D.	.07	trace	.17	.21
6P	1.89	21.67	3.13	5.93	66.23	1.44	.36	.32	.00	.26	.10	.11	.17	.18
6Q	1.88	21.73	3.11	5.85	66.26	1.48	.47	.23	.03	N. D.	.08	.08	.12	.23
3S	1.88	22.72	2.71	5.09	64.19	4.10	.16	.03	.00	N. D.	.35	trace	.14	.18
3P	2.40	22.35	2.24	5.37	63.47	3.99	.38	.11	.39	.50	.63	.20	.25	.22
3Q	2.60	22.48	1.98	5.16	63.83	4.03	.37	.04	.66	N. D.	.47	.10	.07	.28
9S	2.51	22.80	2.23	5.59	63.86	4.17	.10	.13	.00	N. D.	.32	.22	N. D.	N. D.
9P	2.51	22.68	2.22	5.56	62.82	4.15	.80	.28	.00	.30	.38	.54	.26	.30
9Q	2.84	22.79	1.97	5.59	63.07	4.17	.85	.11	.23	N. D.	.33	.29	N. D.	N. D.
1S	2.70	21.70	2.21	5.97	64.64	3.08	.38	.50	.00	N. D.	.10	.97	.20	.25
1P	2.71	21.46	2.22	6.03	63.05	3.01	1.21	.68	.00	.31	.10	1.58	.36	.24
1Q	3.00	21.75	1.90	5.71	63.58	3.08	1.53	.49	.30	N. D.	.10	1.11	.19	.19
7S	2.82	21.40	2.35	6.64	64.73	3.44	0.02	.29	.00	N. D.	.34	0.28	.14	.15
7P	2.91	21.12	2.35	6.85	63.81	3.42	.41	.36	.03	.33	.42	.58	.15	.23
7Q	3.47	21.20	1.96	6.80	64.10	3.48	.55	.22	.36	N. D.	.32	.38	.11	.21

[a] Corrected for FeO.
[b] Corrected for TiO_2.
[c] Corrected for free CaO.
[d] N. D.=Not determined.

TABLE 2.—*Comparisons between variously calculated clinker phases*

[Percentages by weight]

No.[a]	Al_2O_3/Fe_2O_3	$3CaO.SiO_2$			$2CaO.SiO_2$			$3CaO.Al_2O_3$			$4CaO.Al_2O_3.Fe_2O_3$				MgO			CaO		Glass					
		Equilibrium [b]	Normal [c]	Microscopically determined [d]	Equilibrium [b]	Normal [c]	Microscopically determined [d]	Equilibrium [b]	Normal [c]	Microscopically determined [d]	Equilibrium [b]	Normal [c]	Microscopically determined		Equilibrium [b]	Normal [c]	Microscopically determined [d]	Analytically determined [d]	Microscopically determined	Heat of solution [e]	Microscopically determined		Prismatic dark interstitial material [d]	Na_2O (analytically determined)	K_2O (analytically determined)
													KOH etch [d]	Water-acid etch [d]							KOH etch [d]	Water-acid etch [d]			
4S	0.65	65	65	68	8	8	5	0.2	0	0	22	22	20	20	4.3	4.2	4.3	0.3	0.2	2	0	0	2	0.41	0.10
4P	.89	48	45	57	21	20	10	4	0	0	16	4	18	24	4.2	3.0	4.3	4.2	2.9	21	6	0	2	.53	.20
4Q	.81	59	56	66	11	11	4	3	0	0	18	4	21	27	4.4	3.0	2.7	1.6	1.6	23	6	0	0.2	.37	.12
11S	.87	66	66	67	14	13	13	3	2	0	15	14	15	15	0.9	0.7	0.8	0.1	0.1	2	1	1	3	.52	.05
11P	.90	64	64	65	15	13	14	4	2	0	15	12	15	17	.8	.4	.6	.2	.1	6	4	3	0	.66	.16
11Q	.95	67	67	73	14	12	10	4	1	0	13	10	10	14	.8	.4	.2	.3	.1	7	7	3	0	.51	.08
2S	.97	63	62	64	14	14	15	5	4	0	16	15	17	17	1.7	1.6	1.3	.1	0.1	1	0	0	3	.27	.37
2P	1.01	56	56	57	17	16	11	5	4	0	16	14	20	26	1.8	1.5	2.2	.8	1.0	5	6	0	3	.33	.71
2Q	1.12	58	58	64	16	13	13	6	0.2	0	15	6	11	19	1.9	0.7	0.7	.9	1.2	20	8	3	0	.24	.30
8S	1.63	54	54	55	24	24	27	8	8	7	9	9	8	8	3.9	3.9	2.9	.1	0	0	0	0	0.2	.15	.25
8P	1.64	52	51	58	26	24	25	8	5	0	9	4	6	8	3.5	2.8	2.2	.6	0.4	11	8	6	1.0	.17	.49
8Q	1.65	52	52	62	26	24	21	8	4	0	9	3	5	8	3.5	2.7	1.8	.8	.5	13	10	7	0	.10	.08
10S	1.68	49	49	45	31	31	39	8	8	4	9	8	9	9	1.3	1.2	0.9	.2	.2	1	2	2	trace	.26	.33
10P	1.68	40	41	44	38	36	41	8	7	0	9	8	7	7	1.3	1.2	.9	2.1	1.9	2	2	2	3	.34	.81
10Q	1.68	41	42	47	37	35	36	8	5	0	9	4	3	9	1.3	1.0	.4	2.0	1.6	11	12	6	0.2	.26	.37
6S	1.88	63	63	71	15	14	9	10	9	6	9	8	11	11	1.4	1.2	.4	0	0.1	4	2	2	0	.07	trace
6P	1.89	61	61	62	16	16	16	11	10	7	10	9	10	10	1.4	1.3	.9	0.4	.7	2	3	3	.6	.10	.11
6Q	1.88	61	61	70	17	14	10	10	6	0	10	2	2	10	1.5	0.6	.2	.5	1.0	15	17	9	0	.08	.08
5S	1.88	50	51	54	27	27	25	9	9	7	8	8	4	4	4.1	4.1	4.0	.2	0.2	0	2	2	4	.35	trace
5P	2.40	49	49	59	27	25	17	10	7	0	7	1	1	2	4.0	3.3	4.1	.4	.4	12	8	7	10	.63	.20
5Q	2.60	52	56	66	26	19	17	10	0	0	6	0	trace	1	4.0	3.0	2.1	.4	.1	18	11	10	5	.47	.10
5S	2.51	48	46	48	31	31	37	11	11	10	7	7	5	5	4.2	4.2	3.8	.1	.3	0	0	0	0	.32	.22
5P	2.51	42	43	49	33	31	34	11	8	9	7	6	6	6	4.2	3.6	3.7	.8	.6	9	7	7	2	.38	.54
5Q	2.84	43	45	52	33	28	32	12	5	0	6	0	trace	5	3.2	3.2	3.2	.9	.8	16	13	9	0	.33	.29

5S	2.51	45	46	45	31	31	37	11	11	10	7	7	5	5	4.2	4.2	2.8	.1	.2	0	0	0	0	.32	.32
5P	2.51	42	43	49	33	31	34	11	8	0	7	2	6	6	4.2	3.6	2.5	.8	.7	9	7	7	2	.38	.54
5Q	2.84	43	45	52	33	28	32	12	5	0	6	0	trace	5	4.2	3.2	2.5	.9	.8	16	13	8	0	.33	.29
1S	2.70	55	55	45	21	21	33	12	12	12	7	7	7	7	3.1	3.1	2.4	.4	.4	0	0	0	0	.1	.97
1P	2.71	50	50	55	24	24	24	12	12	trace	7	6	4	4	3.0	2.9	2.5	1.2	.9	3	1	1	13	.1	1.58
1Q	3.00	52	52	58	23	21	19	12	9	0	6	1	6	6	3.1	2.5	1.1	1.5	.3	10	14	14	2	.1	1.11
7S	2.82	53	53	55	22	21	24	14	13	12	7	6	5	5	3.4	3.3	2.8	0	.1	2	2	2	0.3	.34	0.28
7P	2.91	50	50	46	23	22	27	14	11	2	7	3	2	8	3.4	2.9	4.1	.4	.5	9	12	6	7	.42	.58
7Q	3.47	51	58	61	22	12	18	15	0	0	6	0	trace	4	3.5	1.9	1.7	.6	2.0	26	18	14	0.2	.32	.38

[a] S=Slowly cooled clinker; P=plant clinker; Q=quickly cooled clinker.
[b] Calculated assuming complete equilibrium crystallization with allowance made for free CaO, TiO_2, and FeO.
[c] Calculated assuming normal crystallization to approximated glass content. Allowance made for free CaO, TiO_2, and FeO.
[d] Microscopically determined as the average of 5 traverses on each of 5 polished specimens.
[e] Revised values based on heats of solution of glasses on T_2E, T_2W [14] boundary curves and the 1,400° and 1,450° isotherms.

The corrected chemical analyses of the clinkers studied are given in table 1. The values in this tabulation were used in calculating the results in table 2. It will be noted that in a given clinker the Al_2O_3-Fe_2O_3 ratios generally are lower in the slowly than in the quickly cooled clinkers. This is because the constituents in this ratio were corrected for ferrous oxide. Under conditions of crystalline equilibrium the calculated $3CaO.Al_2O_3$ should increase and the calculated $4CaO.Al_2O_3.Fe_2O_3$ decrease with increased Al_2O_3-Fe_2O_3 ratios. An examination of table 2 shows this to be the case.

But under those conditions of crystallization where significant amounts of glass persist after the cooling of the clinker, there should be less of the phases, $3CaO.Al_2O_3$ and $4CaO.Al_2O_3.Fe_2O_3$, since part of these constituents would remain in the glass. The effects should be more pronounced in the more quickly cooled clinkers. Methods of calculation which take account of this residual glass should show this effect. The values obtained microscopically decrease with increased cooling rate, which indicates that the rate of cooling is a significant factor to be considered in calculating clinker phases.

The columns designated "equilibrium" and "normal" in table 2 contain results derived from chemical analyses by two methods of calculation. Under the subheading "normal" are given the results by the method of L. A. Dahl [13], which are an extension of the derivations published by Lea and Parker [14]. Included in the derivations of Dahl are equations for calculating the phase composition under the assumption that the clinker is at equilibrium down to a temperature when the liquid remaining is just equal to the glass content as determined by the heat-of-solution method. Thus glass as used in the resulting computations is an approximated value, and the remaining crystalline phases are calculated by the equations given. The other method is based upon an assumption of complete equilibrium during the cooling of the clinker [15].

The magnesia is included in the Dahl calculations under the assumption that MgO dissolves in the liquid up to 6 percent [16] and that any MgO remaining crystallizes as periclase. Further modifications will be required when the part played by the alkalies and other minor oxides is known. However, the method represents the best method of calculation from chemical analysis available at this time.

In making the calculations, allowance was made for free CaO, FeO, and TiO_2. Free CaO was subtracted from the total CaO; TiO_2 from Al_2O_3; and FeO as Fe_2O_3 was subtracted from Fe_2O_3 to give the amounts of CaO, Al_2O_3, and Fe_2O_3, respectively, which were assumed to participate in the reactions and were, therefore, used in the calculations. The values given for approximated glass content are revised values based on heats of solution of glass on the T_2W, T_2E boundary curves [4] and the 1,400° and 1,450° C isotherms [13].

Comparisons between clinker minerals variously determined are also made graphically in figures 5, 6 (*A* and *B*), 7 (*A* and *B*), and 8 (*A* and *B*). In each of these figures the clinkers are arranged according to increasing microscopically determined content of the particular component being studied. Each figure shows, in addition to the microscopical values, those values calculated assuming "normal" crystallization and those calculated assuming crystalline equilibrium.

[4] Boundary curves in the quaternary system as discussed by Lea and Parker. See reference [14].

The following abbreviations are used in the figures: $C_2S=2CaO.SiO_2$, $C_3S=3CaO.SiO_2$, $C_3A=3CaO.Al_2O_3$, $C_4AF=4CaO.Al_2O_3.Fe_2O_3$.

In figure 6 (*B*) the amount of total alkalies is compared with increasing prismatic dark interstitial material as determined microscopically because, although the composition of the prismatic dark interstitial material is unknown, there is reason to suspect a connection with the total alkali content of the clinker. Under the assumption of crystalline equilibrium there can be no residual glass; hence glass is not plotted for this condition in figure 7 (*B*).

In general, the figures show a better agreement between microscopically determined values and those calculated assuming "normal" crystallization than between microscopically determined values and

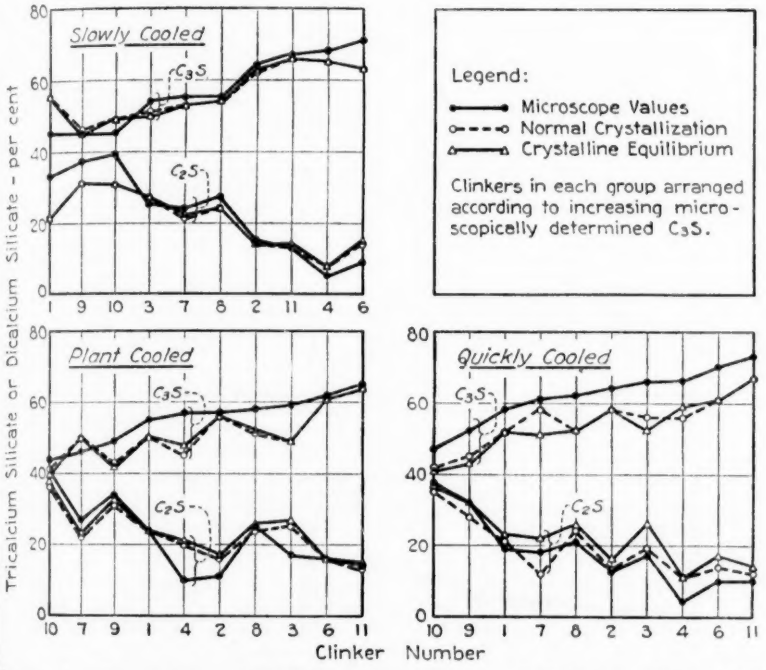

FIGURE 5.—*Comparisons of tricalcium silicate* (C_3S) *and dicalcium silicate* (C_2S) *variously determined.*

those calculated assuming complete equilibrium. For each constituent, agreement is better for slowly cooled clinkers than for either plant-cooled or quickly cooled clinkers. In general, plant-cooled clinkers show better agreement with the calculated phases than quickly cooled clinkers.

Inspection of the tables and figure 5 shows that for the slowly cooled clinkers the values for $3CaO.SiO_2$ and $2CaO.SiO_2$ calculated from chemical analyses agree reasonably well with those derived from microscopical observations. There is a tendency even here for the calculated values for $3CaO.SiO_2$ to be somewhat low and those for $2CaO.SiO_2$ to be somewhat high.

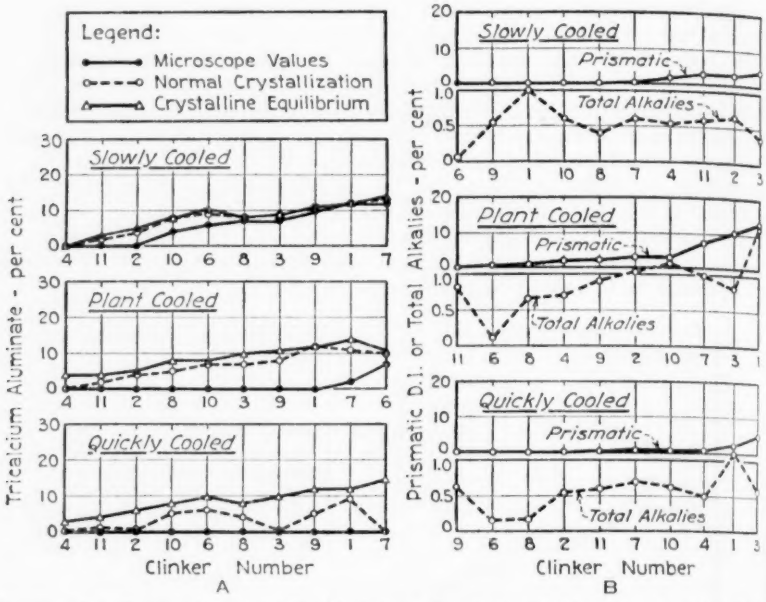

FIGURE 6.—*Comparisons of (A) tricalcium aluminate* (C_3A) *variously determined, and (B) prismatic dark interstitial material and alkalies.*

Clinkers in each group arranged according to increasing microscopically determined C_3A or prismatic dark interstitial material.

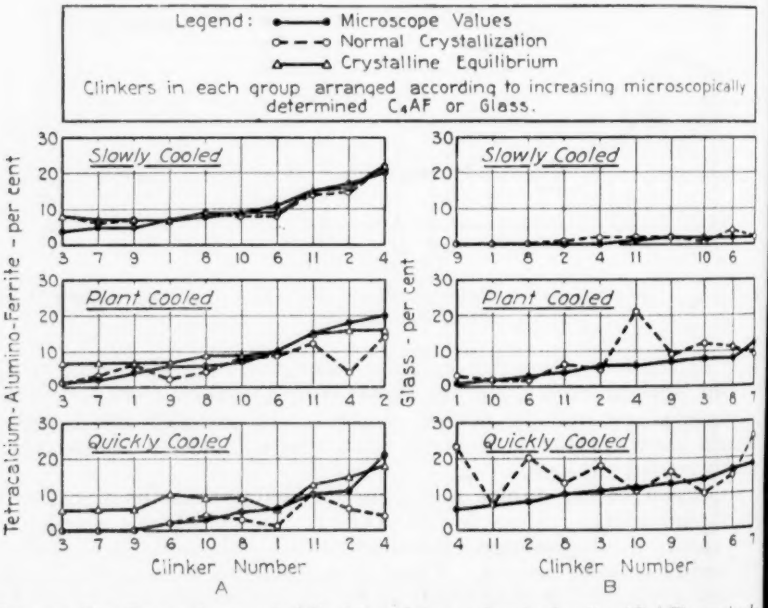

FIGURE 7.—*Comparisons of (A) tetracalcium aluminoferrite* (C_4AF) *variously determined, and (B) glass variously determined.*

This suggests that crystalline equilibrium has not been completely attained, or that the phase identified as $3CaO.SiO_2$ has been augmented by solid solution. In the plant-cooled and the quickly cooled clinkers the above noted tendency becomes marked and definite.

The two dark interstitial crystalline phases etched by water are divided into rectangular and prismatic phases. The rectangular phase agrees optically with tricalcium aluminate while the prismatic phase does not. W. C. Taylor, of this laboratory, suggests that this prismatic phase may be another crystalline form of tricalcium aluminate. It is noteworthy in this connection that the sum of these two microscopically determined crystalline phases, rectangular and pris-

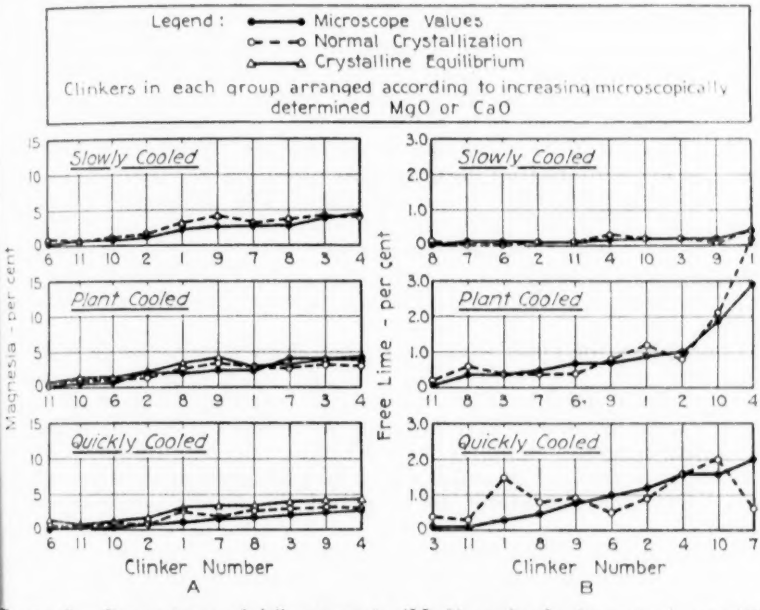

FIGURE 8.—*Comparisons of* (*A*) *magnesia* (MgO) *variously determined, and* (*B*) *free lime* (CaO) *variously determined.*

matic, approaches the values for total tricalcium aluminate as figured by the "normal" crystallization method of calculation. It is Taylor's premise that the rate of cooling and the presence of alkalies have an effect on the type of crystalline dark interstitial material found.

Tricalcium aluminate as a rectangular crystalline phase was found microscopically in all slowly cooled clinkers with Al_2O_3-Fe_2O_3 ratios of 1.63 or greater. Lack of clinkers with Al_2O_3-Fe_2O_3 ratios between 0.97 and 1.63 prevents a more definite statement as to the minimum Al_2O_3-Fe_2O_3 ratio at which this phase appears microscopically in slowly cooled clinkers. Tricalcium aluminate (rectangular) was not found in quickly cooled clinkers and was found in only two plant-cooled clinkers (*6P* and *7P*). In one plant clinker, *6P*, the total alkalies are very low, 0.21 percent; and in the other instance, *7P*, where a small percentage of tricalcium aluminate was found, the Al_2O_3-Fe_2O_3 ratio is the highest, 2.91, of all plant-cooled clinkers

studied. The observed amount of rectangular tricalcium aluminate was always less than that calculated. The negative difference increased as the Al_2O_3-Fe_2O_3 ratio increased and as the cooling became more rapid. Figure 6 (*A*) clearly demonstrates that the formation of rectangular tricalcium aluminate, assuming that the composition was favorable, is dependent upon the rate of cooling.

Since the chemical composition of the prismatic dark interstitial phase is not known, no comparisons were made with the determined microscopical values. Untreated plant clinkers were highest in this prismatic phase and quickly cooled clinkers lowest, possibly because of the higher glass content of the latter. Figure 6 (*B*) points out distinctly that there is little agreement between the total alkalies and the prismatic material. This may mean that the alkalies are only a minor factor in determining whether or not this component appears. It seems from the curves that too slow or too rapid cooling does not favor the formation of the prismatic phase, but rather that some intermediate rate such as in plant operation is favorable.

The amount of tetracalcium aluminoferrite observed microscopically as light interstitial material was often greater than that calculated assuming "normal" crystallization. The differences decreased as the Al_2O_3-Fe_2O_3 ratio increased and increased as the cooling became more rapid. When comparison is made with the calculated values, the agreement is not good for either the Al_2O_3-Fe_2O_3 ratio or the cooling rate change. Their relationships are graphically presented in figure 7 (*A*).

Two values for glass were computed from microscopical observations (see table 2). One value, obtained after etching with water followed by 1 percent HNO_3 in alcohol, represents the glass phase approaching tricalcium aluminate in composition, since it etched in the above reagents similarly to crystalline tricalcium aluminate but to a lesser degree. The other value for glass, obtained after etching with KOH, was considered to represent the total amount of glassy phase.

The amount of glass found microscopically was usually less than that derived from heat of solution data. In clinkers of low Al_2O_3-Fe_2O_3 ratio it was considerably less. In many cases, however, there was fairly good agreement between the amounts of glass found microscopically after etching with KOH and those calculated from heat of solution data.

It is interesting to note in figure 7 (*B*), that as the glass content approached a maximum, as determined by the heat of solution method, the microscope failed to find equivalent amounts. Glass was difficult to determine microscopically, but it is not believed that the large differences shown in some instances were due to failure in identification. There may be some factors not yet recognized, perhaps in both procedures, which when eliminated will permit closer agreement.

Agreement between the values for free lime and magnesia determined microscopically and calculated (analytical values for free lime) was usually good. No consistent variation was observed between these values either with the heat treatment or with the Al_2O_3-Fe_2O_3 ratios. When comparison is made between the values for magnesia

determined microscopically and calculated on the assumption of crystalline equilibrium, the differences between the two methods become important when the cooling is more rapid. This is to be expected since no allowance is made for glass or the solubility of magnesia in it when the composition is calculated on the assumption of crystalline equilibrium. The various values obtained for free lime and magnesia are compared graphically in figure 8 (*A* and *B*).

IV. SUMMARY

The results of the qualitative and quantitative microscopical examination of 10 samples of commercial portland cement clinker with their slowly and quickly cooled counterparts are reported. These are compared with the quantitative phase composition as obtained from chemical analyses by two methods of calculation to show the deviation to be expected among the different methods.

The general appearance of each phase in the clinker is described together with the changes due to differences which had occurred in heat treatment and cooling rate.

It is shown that there is a definite trend toward simplicity of crystal form and clinker structure as the cooling rate increases. Clinkers cooled in the plant have structures that indicate that their rate of cooling lies intermediate between slow and quick cooling.

Comparisons between calculations of phases from microscopical observations and from chemical analyses, according to the presence or absence of glass, show that:

1. The agreement between phases calculated under the assumption of complete equilibrium crystallization and by the microscopical method is better for the slowly cooled clinkers than for either the plant-cooled or quickly cooled clinkers.

2. In general, for all clinkers, the phase compositions calculated with consideration of glass (normal crystallization) agreed better with the microscopically determined phases than did calculations in which complete equilibrium crystallization was assumed.

3. The $3CaO.SiO_2$ found microscopically nearly always exceeds that calculated by either of the other methods.

4. The $2CaO.SiO_2$ microscopically determined was sometimes greater and at other times less than that calculated to be present by either method irrespective of Al_2O_3-Fe_2O_3 ratios.

5. The microscopically determined $3CaO.Al_2O_3$ was always less than that calculated by either of the other methods.

6. The total dark interstitial phases—rectangular, prismatic, and glass—determined microscopically, approached the total tricalcium aluminate calculated on the assumption of crystalline equilibrium.

7. The $4CaO.Al_2O_3.Fe_2O_3$ determined microscopically, in general exceeded that calculated by either of the other methods and showed better agreement for high Al_2O_3-Fe_2O_3 ratios than for low.

8. The glass determined microscopically was in better agreement with values obtained from the heat of solution method for slowly cooled and plant-cooled clinkers than for quickly cooled clinkers.

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U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1359

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SURFACE CHARACTERISTICS OF COTTON FIBERS, AS INDICATED BY ELECTROPHORETIC STUDIES [1]

By Arnold M. Sookne and Milton Harris [2]

ABSTRACT

The surface characteristics of cotton fibers were investigated by a microelectrophoretic technique. Samples of dewaxed cotton, cotton which had been depectinized by treatment with a boiling 1-percent solution of sodium hydroxide for various lengths of time, and pectic substance from cotton gave widely different pH-mobility curves. The curve for pectic substance is characteristic of a highly acidic substance, whereas that for depectinized cotton shows a low order of acidity. The curve for dewaxed cotton appears to be a composite of the curves for cellulose and pectic substance.

The purified cellulose exhibits a reversal of charge below pH 2.5, and accordingly is isoelectric at that pH. It is shown that the reversal of charge has not resulted from irreversible changes produced in the fiber during immersion in the dilute solutions of acid used in the present investigation.

CONTENTS

	Page
I. Introduction	65
II. Materials and methods	66
1. Materials	66
2. Methods	66
III. Experiments and discussion	67
IV. References	69

I. INTRODUCTION

Recent studies on cotton have indicated that the pectic substance occurs principally on the surface of the fiber as part of the primary cell wall [1, 2, 3].[3] Although this substance is present to the extent of only approximately 1 percent, it nevertheless accounts for about 85 percent of the acidic groups in mature fibers. The remainder of the acidic groups, about 15 percent, is presumably associated with the cellulose itself [4]. The highly acidic nature and the location of the pectic substance in the naturally occurring fibers would be expected to influence greatly a number of the properties of the fiber, especially those dependent on surface characteristics. These surface characteristics are of considerable importance in a number of industrial processes, as, for example, the scouring, dyeing, and finishing of textile materials.

The electrophoretic technique has been shown in this laboratory to be a useful tool for characterizing and distinguishing surfaces of different textile fibers or of fibers of which the surfaces have been altered by different chemical treatments [5, 6]. Since it would be

[1] This paper was presented before the Cellulose Division at the 100th meeting of the American Chemical Society, Detroit, Mich.

[2] Research Associates at the National Bureau of Standards, representing the Textile Foundation.

[3] Figures in brackets indicate the literature references at the end of this paper.

expected that the surface of a cotton fiber might also be appreciably changed by treatments which are known to remove pectic substance, it appeared that electrophoretic measurements would be of considerable aid in evaluating such changes.

II. MATERIALS AND METHODS

1. MATERIALS

Raw cotton was extracted with alcohol at room temperature for 24 hours, and then with ether for 24 hours. This will henceforth be described as "dewaxed cotton."

A portion of the dewaxed material was further purified by extraction for 2, 4, 8, or 16 hours with a boiling 1-percent solution of sodium hydroxide, according to the method recommended for the preparation of standard cellulose. The procedure was essentially the same as that described by Corey and Gray [7], except that the apparatus of Worner and Mease was employed [8]. It has been shown by Whistler, Martin, and Harris, that this treatment removes all measurable amounts of pectic substance from cotton [9]. Samples purified in this way will be termed "depectinized cotton."

All of the above samples were reduced to a convenient particle size by grinding them in a laboratory Wiley mill until they passed through a 60-mesh screen. The powder was suspended in water, the larger particles were allowed to settle, and the particles (1 to 5 microns) remaining in the supernatant liquid were used for the measurements.

Pectic substance was obtained by treating dewaxed cotton with a solution of sodium hexametaphosphate, shown elsewhere [10] to separate readily the pectic substance from cotton. The procedure was as follows: 100 g of dewaxed cotton was soaked at room temperature for 7 hours in 1 liter of a 0.5-percent solution of sodium hexametaphosphate at pH 7.9. The liquid was pressed out, and the cotton was soaked overnight in an additional 1-liter portion of the same solution. The combined solutions were dialyzed against running distilled water for 2 days. Hydrochloric acid and potassium chloride were added to portions of the solution until the final ionic strength was 0.02 *M* at pH values from 1.7 to 4.1. Microscopically visible particles suitable for mobility measurements were found to be suspended in the acidified solutions.

2. METHODS

The electrophoretic technique was the same as that used in earlier studies on silk [5] and wool [6] fibers. An Abramson microelectrophoresis cell was used for the measurement of electric mobility [11]. The methods suggested by Moyer were followed in detail [12]. When the mobilities were very low, which was the case for all of the depectinized samples, the velocities of the particles were measured in successive layers from the top to the bottom of the cell, and the mobility was evaluated by graphical integration of the curve obtained by plotting velocity against depth [11].

Preliminary measurements showed that throughout the range of pH investigated, there was no appreciable change of the mobility of the pectic substance or of the dewaxed or depectinized cotton when suspensions were allowed to stand from 15 minutes to 24 hours before mobility measurements were made.

The pH values of the suspensions were measured with a McInnes and Belcher-type glass electrode and a vacuum-tube potentiometer, using a cathode-ray tube as null indicator. The pH values were referred to potassium acid phthalate, 0.05 *M*, to which was assigned a pH value of 4.01 [13].

III. EXPERIMENTS AND DISCUSSION

Curve 5, figure 1, shows the pH-mobility curve for pectic substance. The curve is typical of that of a highly acidic substance, since the particles exhibit a large negative charge even at pH 1.7. This is consistent with the results of an earlier investigation, which showed that the entire uronic acid-carboxyl content of the pectic substance was present in the form of titratable carboxyl groups [4]. The pH-

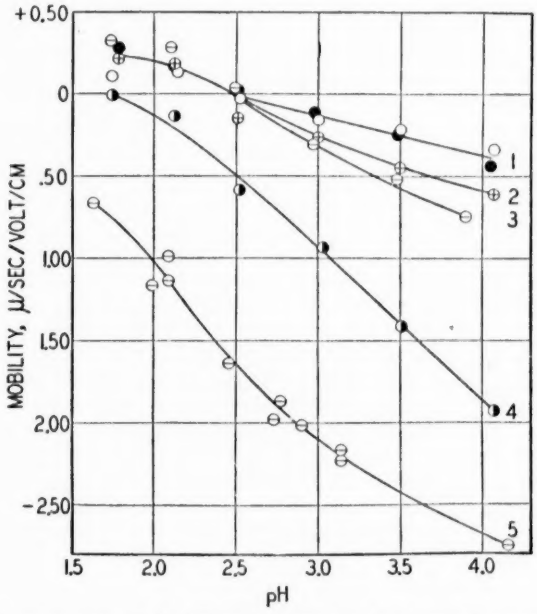

FIGURE 1.—*A comparison of the* pH-*mobility curves for dewaxed cotton, depectinized cotton, and pectic substance from cotton.*

Curve 5 represents the mobility of the pectic substance. Curve 4 is that for dewaxed cotton. Curve 3 is that for cotton treated with boiling 1-percent NaOH for 2 hours. Curve 2 is for cotton similarly treated for 4 hours. Curve 1 is for cotton treated for 8 (open circles) and for 16 hours (filled circles).

mobility curve for dewaxed cotton (curve 4) is similar in shape to that for the pectic substance, but the material is shown by the shift in the curve along the axis of ordinates to be less acidic than the pectic substance. If the particles of dewaxed cotton were completely coated with pectic substance, a curve identical with curve 5 would have been obtained. The results suggest that cutting the fibers exposes new surfaces which are presumably cellulosic, and since these are much less acidic than the pectic substance itself, the number of acidic groups per unit surface has accordingly been decreased. It would appear then

that curve 4 is a composite of the curves for the highly acidic pectic substance and the much less acidic cellulose.

The pH-mobility curve of a sample of depectinized cotton, prepared by treating dewaxed cotton for 2 hours with a boiling 1-percent solution of alkali, is shown in curve 3. Its position relative to the curve for dewaxed cotton indicates the removal of an acidic component. Slight further shifts in the pH-mobility curve were caused by 4 hours (curve 2) and 8 hours (curve 1) of extraction with the alkali, but these last effects are much smaller. A sample treated for 16 hours gave no further change in the pH-mobility curve (curve 1).

The small shifts in the positions of the pH-mobility curves for samples of cotton treated for 4 and for 8 hours were somewhat surprising, especially since earlier determinations of uronic acid [9] as well as titration studies [4] had indicated that essentially all of the pectic substance was removed from the fiber during the 2-hour treatment with alkali. It must be pointed out, however, that the electrophoretic measurements are much more sensitive to small changes than either of the above techniques and therefore the possibility that removal of the last traces of pectic substance during treatment with alkali for 2 hours is not complete, cannot be ruled out. If the data are interpreted in this light, then they must also be taken to indicate that the samples treated for 8 and for 16 hours are essentially free of pectic substance.

Two alternative explanations for these shifts may be advanced. First, the continued treatment with alkali may remove a small amount of surface material which contains no carboxyl groups but which is more electronegative than the cellulose itself. Second, the continued treatment with alkali may alter the physical structure of the fiber, with a resultant change in the mobility curve. Numerous instances exist in which a physical change, such as alteration of the degree of orientation, has been shown to change the electrokinetic properties of substances. Kanamaru, for example, has observed that the zeta potentials are different for rayons spun of the same material, but of varying degrees of orientation [15], and a similar observation has been made on nylon by Sookne and Harris [14]. Harrison found a large decrease in the (negative) zeta potential of cotton after mercerization [16], and since the small changes observed in the present investigation are in the same direction, they could possibly be caused by alteration of the physical character of the fiber surface.

It will be noted that the depectinized samples of cotton exhibit reversal of charge below about pH 2.5 and accordingly are isoelectric at that pH. However, it has been reported [17] that cellulose has no true isoelectric point and that reversal of the charge in the more acid solutions resulted from hydrolysis at the surface of the fiber. Although these conclusions arose from investigations on wood cellulose, it nevertheless appeared advisable to determine whether any irreversible effects had been produced under the conditions of the present studies. For this purpose, the following experiments were performed. 1.5-g samples of ground, depectinized (8 hour) cotton were soaked in 400-ml portions of hydrochloric acid–potassium chloride solutions (0.02 *M* ionic strength) having pH values of 1.7, 2.5, and 3.3. These solutions were identical with those used in obtaining the data shown in figure 1. After 1 hour, the samples were filtered off on a sintered glass funnel and thoroughly washed with running distilled water. Water sus-

pensions of each of the three samples as well as of a sample of the untreated, depectinized cotton were then prepared and sufficient acetic acid and sodium acetate added to bring the pH value of each solution to 5.6 and the ionic strength to 0.005 *M*. The samples were allowed to remain in contact with the buffer solutions for 24 hours, after which the mobilities of the particles were measured. No significant differences between the acid-treated and untreated samples were found and therefore it was concluded that no irreversible changes in the surface potential of cotton were produced by the dilute solutions of acid employed in the present work.

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COMBINATION OF SILK FIBROIN WITH ACID AND WITH BASE

By Leland F. Gleysteen and Milton Harris [1]

ABSTRACT

A study was made of the dependence on pH of the amounts of hydrochloric acid and of potassium hydroxide that are taken up by silk fibroin at 0° C. The effect of added potassium chloride on this dependence was also investigated, and was shown to be the binding of an increased quantity of acid or base at a given pH.

The maximum acid-combining capacity of silk fibroin is 0.13 milliequivalent per gram; the maximum base-binding capacity is greater than 0.90 milliequivalent per gram. The presence of 0.13 to 0.17 milliequivalent of free carboxyl groups in silk fibroin is estimated from the titration curve. The great amount of base bound can be accounted for only if the phenolic hydroxyl groups of tyrosine take part in the equilibria with base. Further evidence that these groups bind base is provided by the greatly decreased amount of base bound by methylated fibroin.

CONTENTS

	Page
I. Introduction	71
II. Experimental procedure	72
1. Materials	72
(*a*) Fibroin	72
(*b*) Methylated fibroin	72
2. Methods	73
(*a*) Correction for ash	72
(*b*) Determination of moisture	73
(*c*) Correction for sorption of water	73
(*d*) Titration with acid	74
(*e*) Titration with base	74
(*f*) Determination of pH	75
(*g*) Temperature control	75
III. Results and discussion	75
IV. References	79

I. INTRODUCTION

Many of the chemical and physical properties of a protein fiber are intimately related to the number and arrangement of those groups which bind acid or base. A study of the combination of acid and of base with silk fibroin was therefore undertaken as part of an extensive program for the investigation of the acidic and basic nature of textile fibers.

The manner in which the titration curves of the insoluble proteins, and especially of wool, differ from those of the soluble proteins has been discussed by Speakman and Hirst [1], [2] by Lloyd and Bidder [2]

[1] Research Associates at the National Bureau of Standards, representing the Textile Foundation.
[2] Figures in brackets indicate the literature references at the end of this paper.

and, more recently, by Steinhardt and Harris [3]. The titration of silk fibroin is, in some respects, similar to the titration of wool, but differs in other respects because of decided differences in the number and kinds of constituent amino acid residues. The published analyses of silk [4] indicate that fibroin contains relatively small quantities of the dibasic amino acids arginine, lysine, and histidine, all of which would be expected to bind acid, and an appreciable quantity of one diacidic amino acid, tyrosine, which would be expected to bind base unless its phenolic hydroxyl group is blocked in some way.

The data for proteins do not provide an unequivocal indication of the availability of the hydroxyl groups of tyrosine for binding base. Recent work, however, on the reaction of diazomethane with silk and a number of other proteins indicates that the hydroxyl groups of tyrosine in these substances are probably free.

The relatively high content of tyrosine in fibroin made it seem probable that the role of the hydroxyl groups in acid-base equilibria would be revealed by consideration of the titration data. Since the methylation of these groups can now be readily brought about [5], a comparison of the titration curves of untreated and of methylated fibroin should indicate even more clearly the part taken by the phenolic hydroxyl groups in the binding of base by fibroin.

II. EXPERIMENTAL PROCEDURE

1. MATERIALS

(a) FIBROIN

Raw, white, Japanese silk which had not been previously treated except for the reeling operation was extracted for 48 hours with alcohol and for 24 hours with ether, both at room temperature, and was finally washed in water. The silk was degummed by treatment with a commercial enzyme preparation, Enzo.[3] The degumming bath contained 5 g of Enzo per liter and was maintained at a temperature of 65° C. The ratio of silk to solution was about 1:40. Each lot of silk was given three consecutive treatments of half an hour each with constant agitation; after each treatment the silk was quickly rinsed in boiling water and was then thoroughly washed in water at room temperature. In order to assure complete degumming, it was found necessary to prevent the silk from becoming tightly matted. Determinations of loss of weight showed that three treatments of half an hour each, and subsequent washings were sufficient to bring the material to constant weight. The loss of weight on degumming corresponded to the loss reported by Rutherford and Harris [6] for silk of the same lot degummed by boiling in soap solutions.

(b) METHYLATED FIBROIN

Fibroin was methylated with diazomethane as described by Rutherford, Patterson, and Harris [5]. Analysis of the samples for tyrosine by the method of Lugg [7] showed that the tyrosine content

[3] Thanks are due the Wallerstein Laboratories, New York, N. Y., for the enzyme preparation used in this work.

had been reduced from 12.0 to 2.3 percent, and analysis for methoxyl groups by the method of Vieböch and Brecker [8] showed that the methoxyl content was 2.37 percent.

2. METHODS

(a) CORRECTION FOR ASH

The degummed silk contained some base, already bound, and yields an alkaline ash. This alkali affects the extent to which acid or base is sorbed from the solution by the fibroin. The hydrogen-ion equivalence of the ash was determined by an electrodialytic method which has been described elsewhere [9]. The degummed and washed fibroin had an ash content of the order of 0.1 milliequivalent per gram (M-eq/g). In order to reduce the ash content to a lower value the fibroin was electrodialyzed for 24 hours. By this means, the hydrogen-ion equivalence of the ash was reduced to 0.01 to 0.02 M-eq/g. The titration data were corrected for the effect of this residual ash by subtracting the hydrogen-ion equivalence of the ash from the experimentally determined quantity of acid bound or by adding it to the quantity of base bound.

(b) DETERMINATION OF MOISTURE

All the samples were conditioned at 21° C and 65-percent relative humidity before weighing. The moisture content of the fibers was determined by drying representative samples for 2 hours in a vacuum oven at 105° C. All titration data in this paper are expressed as milliequivalents of acid or of base per gram of dry fibroin.

(c) CORRECTION FOR SORPTION OF WATER

In the determination of the titration curves of hygroscopic fibrous materials some investigators have considered the total moisture content of the sample of fibers, at the moment immediately preceding immersion in the solution, as a quantity which should be added to the free water of the system. That is to say, all the water in the system, including that introduced in the fiber phase, has sometimes been regarded as being available for dilution of the solute. However, many workers have recognized, on the basis of direct experimental evidence, that the concentration of an aqueous solution of a solute which is not bound to the fiber by strong chemical or physical forces is *increased* when a sample of fibers of low moisture content is introduced into the solution. Presumably such an increase in the concentration of the solution is due to the selective sorption of water by the fibers. It is also assumed that such sorption effects occur in solutions of acids and bases and decrease the quantity of water that is available for dilution of the acid or base. Since the acid and base binding capacities, as determined in the present investigation, are calculated from changes of titer, and since the change in the titer of the solutions will depend upon the selective sorption of water as well as upon the quantity of acid or base bound, a correction must be applied for the sorption of water.

The manner of applying this correction term is discussed in detail by Sookne and Harris [10]. In the present investigation the extent of selective sorption of water was investigated by a polarimetric

method. The highly optically active disaccharide trehalose was used as a reference substance. It was assumed that the trehalose was not sorbed by the fiber. A weighed quantity, 5 g, of fibroin of known moisture content was immersed in the smallest convenient volume, 60 ml, of trehalose solution, which was 0.05 *N* with respect to hydrochloric acid, and then placed in the constant temperature bath at 0° C. After 24 hours, aliquots were withdrawn from the stock solution and from the solution in equilibrium with the fibers, and the rotations were measured in a saccharimeter at 20° C. The rotations of the original and of the final solutions were compared, and the difference was interpreted as a measure of the increase of the concentration of the solution with respect to trehalose, which resulted from the sorption of water by the fibroin. The mean result for a pair of duplicate determinations is shown in table 1.

TABLE 1.—*Selective sorption of water by silk fibroin*

Dry weight of fibroin	g	4.57
Moisture content per gram of dry fibroin	g	0.095
Change in rotation of solution	%	1.26
Original volume of solution	ml	60.0
Water selectively sorbed	g	0.756
Water selectively sorbed per gram	g	.165
Total water in fiber not available for dilution of solute (grams per gram of dry fibroin)	g	.26

(d) TITRATION WITH ACID

Samples of fibroin weighing either 3.00 or 4.00 g and containing about 9.2 percent of moisture were placed in 100-ml portions of acid solutions at 0° C. The solutions contained either varying amounts of hydrochloric acid alone or varying amounts of potassium chloride and hydrochloric acid so adjusted as to bring the total ionic strength, at equilibrium, to 0.2 *M*. Aliquots of the original solutions and of the solutions which had come to equilibrium with the fibroin were titrated with standard sodium hydroxide solutions, using bromcresol purple as the indicator. The change in titer, together with the dry weight of the sample and the correction for selective sorption of water, permits the calculation of the quantity of acid bound per gram of dry fibroin.

To determine whether sufficient time had been allowed for the attainment of equilibrium and whether appreciable acid hydrolysis had occurred, aliquots were withdrawn from the acid solutions which had been in contact with the fibroin for periods of 2, 3, and 4 days. The results indicate that equilibrium is attained within 48 hours and that no appreciable hydrolysis occurs within 4 days at 0° C in solutions up to 0.1 *N* with respect to hydrochloric acid.

(e) TITRATION WITH BASE

Titrations with base were carried out in a manner analogous to the method used for acid titrations, with the addition of precautions to prevent errors resulting from exposure of the solutions to atmospheres containing carbon dioxide. The alkaline solutions were made up from a stock solution of potassium hydroxide of very low carbonate content and a stock solution of potassium chloride of very low carbon dioxide content, by dilution with freshly boiled distilled water.

To determine the time required to attain equilibrium and to investigate the question of the alkaline hydrolysis of the protein material, a number of samples were immersed in potassium hydroxide solutions at pH 12 for various periods of time. The results indicate that equilibrium is attained in about 24 hours at 0° C and that no appreciable hydrolysis seems to have occurred within 72 hours at this temperature, as the quantity of base bound reached a constant value and the Nessler test did not reveal the presence of any nitrogen in solution. In all subsequent experiments the samples were allowed to remain in the solution for 48 hours before aliquots were withdrawn for titration.

(f) DETERMINATION OF pH

The pH values of the solutions were determined with a glass electrode following the method used by Steinhardt and Harris [3].

(g) TEMPERATURE CONTROL

The solutions were maintained at a temperature of 0° C by immersion in a refrigerated bath containing water and ice.

III. RESULTS AND DISCUSSION

The amounts of hydrochloric acid and of potassium hydroxide bound by fibroin at 0° C at different pH values (at equilibrium) are given in table 2 and are shown graphically in figure 1. The titration

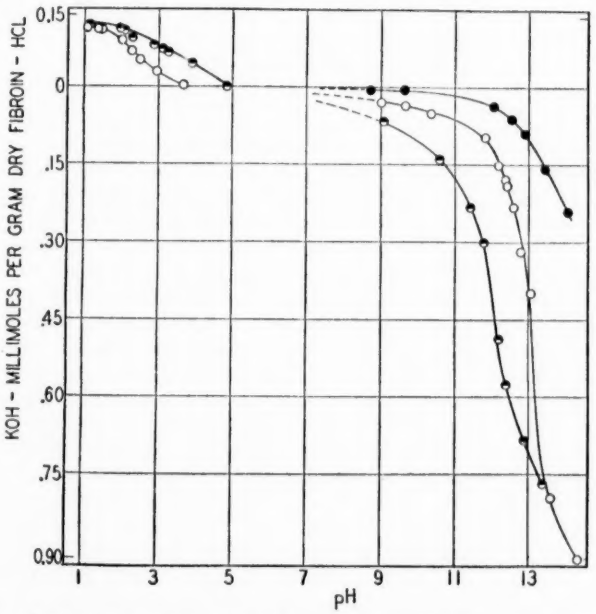

FIGURE 1.—*Combination of silk fibroin with hydrochloric acid and potassium hydroxide as a function of pH*

○ No salt.
◎ Ionic strength 0.2 *M*.
● Methylated fibroin, no salt.

curve for hydrochloric acid in the absence of salt (open circles) drops steeply from a maximum of about 0.13 *M*-eq/g near pH 1 and appears to reach the base line at about pH 3.9. It should be noted that, because of the shallow slope of the curve as it approaches the base line, any error in the ash correction or in the titration data will affect the position of the point at which combination with acid appears to begin.

TABLE 2.—*Amounts of acid and base bound by silk fibroin at 0° C*

pH	Acid bound	pH	Base bound
NO SALT PRESENT			
	M-eq/g		*M-eq/g*
1.083	0.132	9.01	0.033
1.131	.130	9.63	.034
1.553	.117	10.40	.052
2.046	.091	12.18	.147
2.331	.074	12.43	.205
2.468	.044	12.76	.314
2.950	.031	13.10	.395
3.522	.003	13.61	.798
		14.25	.904
IONIC STRENGTH 0.20			
1.187	0.136	9.10	0.070
1.822	.119	10.61	.139
2.101	.115	11.44	.228
2.360	.092	11.80	.298
2.875	.080	12.24	.487
3.138	.077	12.44	.581
3.276	.057	12.89	.686
3.968	.049	13.48	.767
4.633	.001		

In solutions of ionic strength 0.2 (half-filled circles), acid combination appears to begin at about pH 4.8. The effect of keeping the solution at constant ionic strength 0.2 is clearly indicated by the figure. At the lower values of pH the curves tend to join each other, as indeed they must if the curve for constant ionic strength be extended to that point at which no salt is present. As in the case of wool [3], the central portion of both the acid and the alkaline regions of the curve for solutions of constant ionic strength is not as steep as the curve for solutions without salt, and a greater amount of acid or base is bound at a given pH. The effect of the presence of salt on the slope and position of the titration curve is greater than could reasonably be accounted for by the influence of the salt on the dissociation constants of the groups which are titrated. It will be observed that for the preservation of electrical neutrality in the solutions and in the fibers it is necessary that the fibers should bind an anion with every proton and a cation with every hydroxyl ion. A few determinations of the chloride titer of the acid solutions served to indicate that chloride ions are bound in quantities approximately equivalent to the amount of hydrogen ion bound. A detailed discussion of the effect of salt and a theoretical treatment of the titration data for another fibrous protein, wool, have been given elsewhere by Steinhardt and Harris [3], who showed that the quantity of acid bound depends upon the concentra-

tion of anions as well as on the concentration of hydrogen ions, and that the quantity of base bound similarly depends on the concentration of cations as well as on hydroxyl ions. They explained the direct dependence on anion, or cation, concentration on the basis of the assumption that when the protein combines with hydrogen ions it also forms partially dissociated stoichiometric complexes with anions and when it combines with hydroxyl ions it forms similar complexes with cations. These conclusions now appear to be applicable to silk fibroin as well.

The titration curve for fibroin obtained from these experiments at 0° C differs in several respects from that given by Lloyd and Bidder [2]. At the higher concentrations of acid Lloyd and Bidder indicate that rapidly and continuously increasing amounts of acid are bound as pH decreases, the highest value shown being some 0.3 *M*-eq/g at pH 1; the data of the present investigation tend toward a maximum of about 0.13 *M*-eq/g in the region of pH 1. This difference cannot be ascribed to the effects of ash because Lloyd and Bidder report an ash content of only 0.02 percent which, on the assumption of an equivalent weight of 40 for the ash, as found in the fibroin used in the present investigation, would amount to about 0.005 *M*-eq/g. The discrepancy may be due in part to some decomposition of the fibroin at the higher temperatures at which Lloyd and Bidder worked. The alkaline branches of the curves are less dissimilar and, in this case, at least, a part of the difference may be attributed to a temperature effect. It has been shown that temperature appreciably influences the binding of base by wool but has very little effect on the binding of acid [11].

It is recognized that the acid- and base-combining capacities of proteins may usually be correlated with their contents of diacidic and dibasic amino acids [12]. The published analytical data on the composition of fibroin are given in table 3 [4, 13]. The maximum quantity of acid bound by fibroin, 0.13 *M*-eq/g, is nearly twice the sum of the reported contents of arginine and lysine. Such a discrepancy is not unexpected, since in the isolation of small quantities of amino acids from protein hydrolysates the analytical results invariably are low.

TABLE 3.—*Amino acid composition of fibroin*

Amino acid	Percentage	*M*-eq/g
Glycine [a]	43.8	5.84
Alanine [a]	26.4	2.97
Tyrosine [a]	13.2	0.73
Arginine [a]	0.95	.055
Lysine [b]	.25	.018
Histidine [b]	.07	.005

[a] Reference [4].
[b] Reference [13].

In the literature no values whatever are reported for dicarboxylic acids in silk fibroin. The nature of the titration curve, however, is such as to suggest that dicarboxylic acid residues are probably present. The total amount of acid plus base bound between pH 1 and pH 7 to 8 (in which range the —COOH groups are known to undergo dissociation), which is not less than 0.13 and may be as much as 0.17

M-eq/g in the case of silk fibroin, may be regarded as a measure of the total number of free carboxyl groups in the protein. Previous evidence that silk fibroin contains free carboxyl groups was given by Rutherford, Patterson, and Harris [5], who infer the presence of about 0.2 *M*-eq/g of free carboxyl groups in the untreated fibroin from the analyses of methylated fibroin for unmethylated tyrosine and for methoxyl groups. The latter estimate lends support to the interpretation of the quantity of acid plus base bound between pH 1 and 8 as representing the free carboxyl content of fibroin.

The amount of base bound in the strongly alkaline region, that is at pH greater than 11, greatly exceeds the content of free carboxyl groups and can be accounted for only by postulating that the phenolic groups of the tyrosine take part in the binding of base. This result is not unexpected, as Rutherford, Patterson, and Harris [5] concluded, on the basis of their study of the methylation of fibroin with diazomethane, that the hydroxyl groups are free. The greatest amount of base bound in the range covered by this investigation, 0.90 *M*-eq/g, is somewhat more than the tyrosine alone would account for and is, fortuitously, equal to the tyrosine content plus the estimated content of free carboxyl groups. Presumably higher amounts of base would be bound at higher pH values at which, however, the estimation of base bound and of pH would be attended by such large errors as to make the experimental data unreliable.

Additional evidence for the conclusion that the phenolic hydroxyl groups of tyrosine bind base is provided by the data on the combination of methylated fibroin with potassium hydroxide, given in table 4. In this material all but approximately one-fifth of the tyrosine had been methylated. The titration curve (solid circles, fig. 1), is shifted toward higher pH. Up to pH 9.5 very little base is bound, and at any given pH the amount bound is very much less than in the case of the unmethylated fibroin. This greatly decreased base-binding capacity of the methylated fibroin lends support to the interpretation of the very steep portion of the curves for nonmethylated fibroin as being due to the titration of the phenolic hydroxyl groups of tyrosine.

TABLE 4.—*Amounts of base bound by methylated fibroin at 0°C*

pH	Base bound
	M-q/g
8.74	0.005
9.48	.005
12.15	.037
12.55	.061
12.84	.091
13.47	.166
14.14	.283

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THERMAL EXPANSION OF ELECTROLYTIC CHROMIUM

By Peter Hidnert

ABSTRACT

The linear thermal expansion of two samples of electrolytic chromium was investigated at various temperatures between −105° and +715° C. During the first heating or heatings, when hydrogen presumably was being evolved, the samples contracted in an irregular manner. After a few heatings, however, the irregularities disappeared and smooth expansion curves were obtained. It appears also, that the linear thermal expansion of electrolytic chromium, when it is first heated, may be affected by variables such as the temperature, time and rate of heating, previous treatment, etc. The following equations were derived for the length, L_t, at any temperature, t, between −100° and +700° C, and for the coefficient of expansion, a_t, at any temperature, t, between −75° and +650° C:

$$L_t = L_0[1 + (5.88t + 0.00774t^2 - 0.00000388t^3)10^{-6}]$$

and

$$a_t = (5.88 + 0.01548t - 0.00001163t^2)10^{-6}.$$

The density of the sample of electrolytic chromium containing 99.3 percent of chromium increased 2.4 percent and the volume decreased 2.3 percent, after three cycles of heating to 500° C and cooling to room temperature. The length decreased 1.1 percent.

CONTENTS

		Page
I.	Introduction	81
II.	Materials investigated	82
III.	Apparatus	82
IV.	Results	83
V.	Discussion	89
VI.	Summary and conclusions	90
VII.	References	91

I. INTRODUCTION

The main objects of the use of chromium electroplating are the prolongation of the life of metal or alloy parts subject to wear or temperature and the production of a decorative effect. The porosity of new deposits of electroplated chromium coatings has been observed to increase for several weeks or on heating [1],[1] and the development of cracks in chromium plating during atmospheric exposure at ordinary temperatures has been discussed by several observers [2, 3]. Determinations of the linear thermal expansion of electrolytic chromium therefore appeared to be desirable for a possible explanation of the behavior of chromium platings, particularly when heated.

Disch [4] appears to be the first investigator who published data on the linear thermal expansion of chromium. He obtained the sample of chromium from Firma Th. Goldschmidt A.-G. in Essen,

[1] The numbers in brackets indicate the references at the end of this paper.

Germany, but he did not report any information about its chemical composition, preparation, or treatment. In 1922 Chevenard [5] published a curve indicating the coefficients of linear thermal expansion of chromium containing 98.3 percent of chromium. He also failed to give information about its preparation or treatment.

In 1931 Hidnert [6] presented to the American Physical Society data on the linear thermal expansion of a sample of electrolytic chromium containing 99.3 percent of chromium. The present paper includes additional data on the thermal expansion of this sample and on another sample of electrolytic chromium.

II. MATERIALS INVESTIGATED

Table 1 gives the chemical composition and the density of the two samples of electrolytic chromium investigated. Sample 1359A was prepared at the National Bureau of Standards by G. E. Renfro, and sample 1328I was prepared by Union Carbide & Carbon Research Laboratories, Inc., New York, N. Y.

It was reported in 1931 [6] that chromium produced at the National Bureau of Standards, under conditions similar to those for sample 1359A, was found to contain about 0.1 percent of hydrogen.

The data in table 1 fail to account for the remaining 0.6 percent in sample 1359A or the 1.2 percent in sample 1328I. Extensive investigation would be required to decide whether these undetermined portions consisted of (a) hydrogen in greater amount than was found by analysis of similar specimens, or (b) oxygen in some form, such as Cr_2O_3 or $Cr(OH)_3$.

TABLE 1.—*Chemical composition and density of electrolytic chromium*

Sample	Material	Chemical composition [a]						Density [b]
		Cr	Fe	Si	Mn	Pb	Cu	
		%	%	%	%	%	%	g/cm³
1359A	Tube, length 300 mm, outside diameter 9 mm, inside diameter 8 mm.	99.3	0.002	0.002	(e)	(e)	(e)	{6.934 [d] 7.103 [e]
1328I	Three pieces, each 8 mm in length	98.7	.003	(e, f)	(e)	(e)	(e)	7.03 [g]

[a] Determined by R. M. Fowler, formerly of the National Bureau of Standards.
[b] Determined by E. Hill and S. Alpher, formerly of the National Bureau of Standards.
[c] Not detected.
[d] At 22.5° C before first expansion test (see fig. 1).
[e] At 22.3° C after third expansion test (see fig. 1).
[f] Spectrographic analysis by C. C. Kiess, of the National Bureau of Standards, indicated traces of Si and C.
[g] At 25° C (on duplicate pieces before heating).

III. APPARATUS

Sample 1359A was investigated at various temperatures between −105° and +706° C with the precision-comparator type of thermal-expansion apparatus described by Souder and Hidnert [7]. Tests 1, 2, 3, 9, and 10 were made with the white furnace shown at the left of figure 1 of their publication. Figure 4 of the same publication shows the details of mounting the sample in the furnace. Tests 4 to 8, inclusive, were made with the oil bath shown at the extreme right of figure 1 of the publication by Souder and Hidnert [7]. Figure 3

of their publication shows the sample, sample holder, and contact fingers for the vertical position wires used in the oil bath.

On account of the small pieces of chromium available for sample 1328I, the interferometer method [8] of measuring thermal expansion was employed. Five tests were made with this method at various temperatures between 21° and 715° C. At each observation, the temperature was kept constant for a sufficiently long time to make certain that the sample had attained temperature equilibrium.

IV. RESULTS

Ten tests were made on the linear thermal expansion of sample 1359A, and five tests were made on sample 1328I. Figure 1 shows the observations obtained in the first three tests on the linear thermal expansion of sample 1359A, and figure 2 shows the observations in the last two tests of this sample. Figure 3 shows the observations obtained in five tests on sample 1328I. Each expansion curve was plotted from a different origin. The dotted portions of some curves indicate that in these regions sufficient observations were not obtained to locate the curves definitely. In each test, the numbers adjoining the observations represent the time, in hours, from the time of the initial observation.

In tests 1 to 3 on sample 1359A (fig. 1), the sample was heated to 500° C and cooled to room temperature in the furnace in an atmosphere of air. During the first heating to 500° C the sample contracted considerably, probably with an evolution of hydrogen.[2] At 500° C, the sample was 0.7 percent shorter than the initial length before heating. On cooling the sample to room temperature, the observations appeared to lie on a smooth curve. After cooling the sample to room temperature it was 1.1 percent shorter than before heating.

The expansion curve obtained in the second heating of sample 1359A is regular except in the neighborhood of 500° C. This slight irregularity was perhaps also accompanied by evolution of hydrogen. The contraction curve obtained on cooling in the second test is regular and lies below the expansion curve.

The expansion curve obtained in the third heating of sample 1359A is smooth. It may therefore be assumed that no appreciable amount of hydrogen was evolved during this heating. The observations on cooling during the third test lie slightly below the expansion curve.

The expansion and contraction curves of the second and third tests of sample 1359A are nearly parallel to the contraction curve of the first test.

The fourth test on sample 1359A between −105° and +100° C, and tests 5 to 8, inclusive, between room temperature and 300° C, were made in the oil bath. The sample was surrounded by pentane at temperatures between −105° and +20° C, and by Renown engine oil at temperatures between 20° and 300° C.

The observations of tests 9 and 10 on sample 1359A shown in figure 2, were obtained in the furnace between room temperature and

[2] A qualitative chemical test was made on duplicate pieces of sample 1328I, and it was found that hydrogen was evolved on heating.

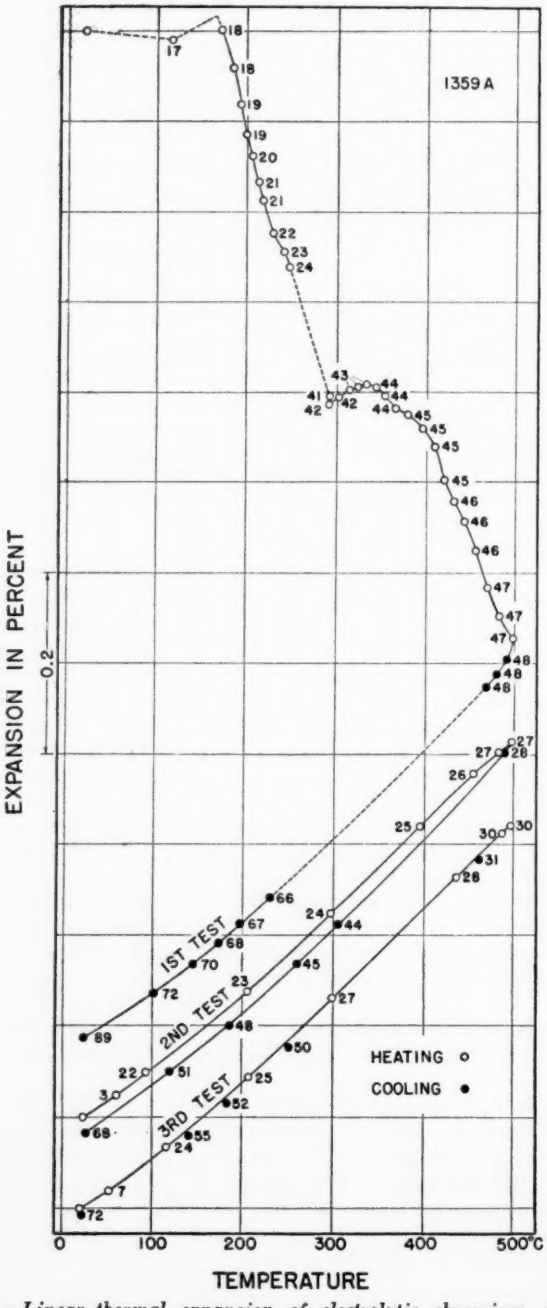

FIGURE 1.—*Linear thermal expansion of electrolytic chromium, 99.3 percent (tests 1 to 3, inclusive).*

Each number adjoining an observation indicates the time, in hours, from the time of the initial observation.

about 700° C. In test 9, the rate of expansion decreased above 500° C, probably with additional evolution of hydrogen. The contraction curve on cooling in test 9 is regular and lies below the expansion curve. The expansion curve in the tenth test is smooth, and the observations on cooling lie slightly below the expansion curve.

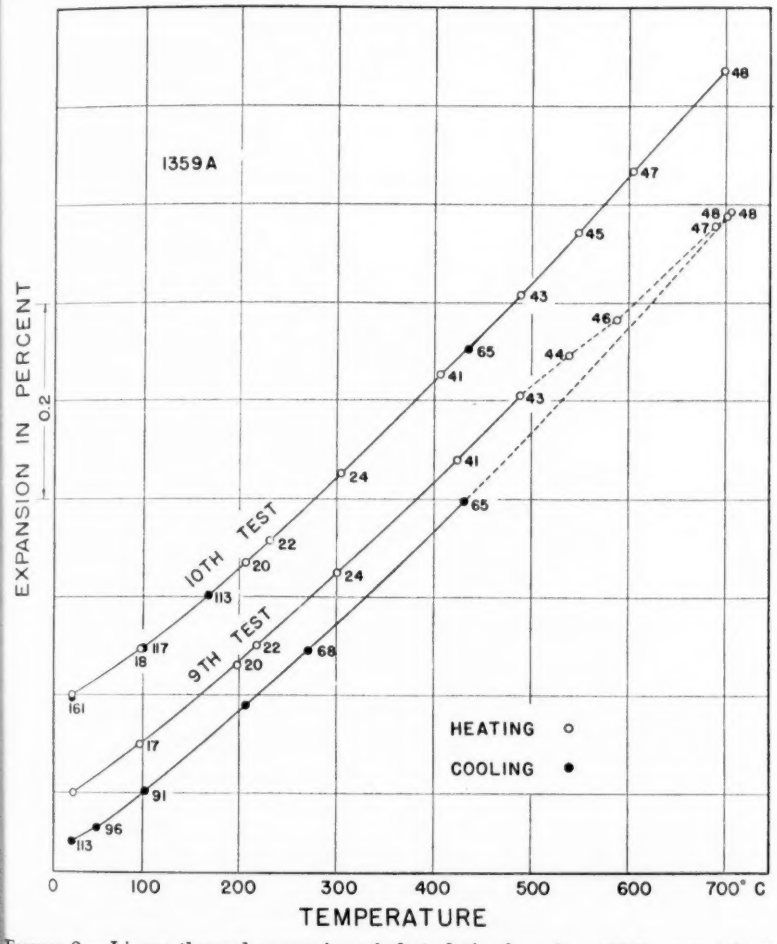

FIGURE 2.—*Linear thermal expansion of electrolytic chromium, 99.3 percent (tests 9 and 10)*

Each number adjoining an observation indicates the time, in hours, from the time of the initial observation.

The observations obtained on sample 1328I in tests 1 to 5 are shown in figure 3. In these tests by the interferometer method, the three pieces of chromium representing the sample were heated in a furnace in an atmosphere of air. During the first heating, the sample contracted in the neighborhood of 300° C. In the second heating, the rate of expansion decreased between 200° and 400° C., and the sample contracted in the neighborhood of 400° C. The sample was heated

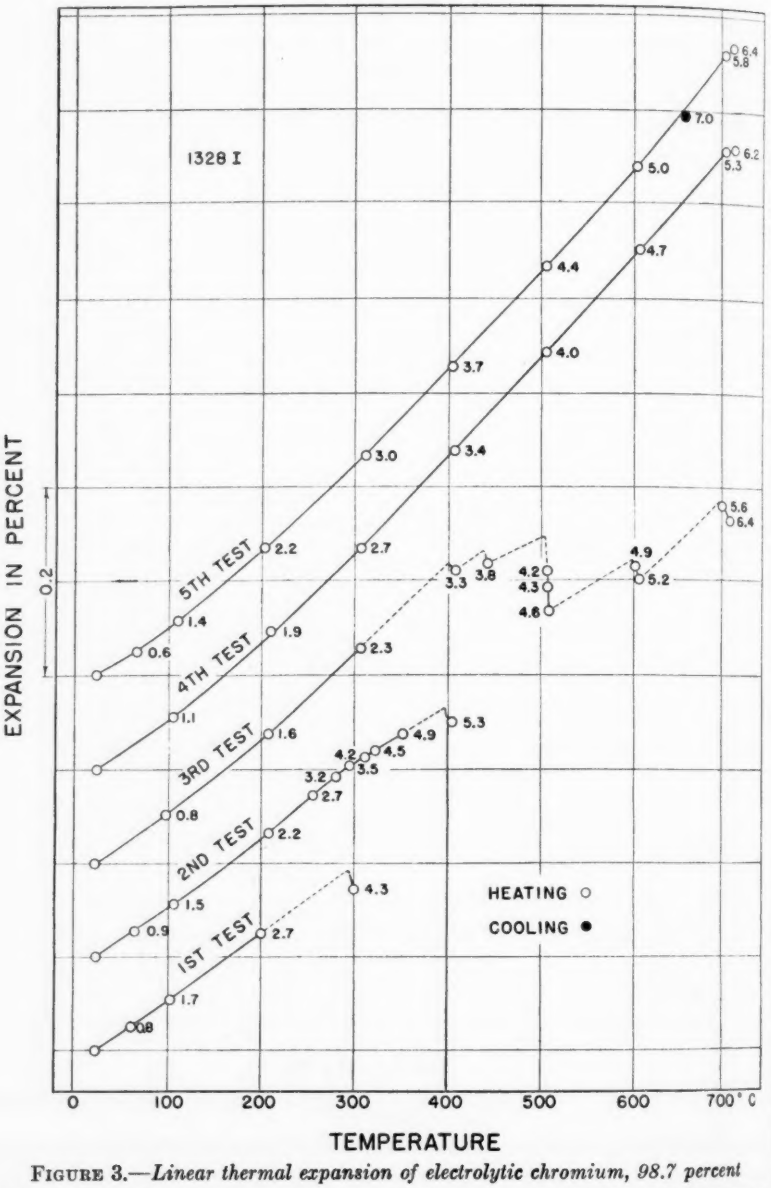

FIGURE 3.—*Linear thermal expansion of electrolytic chromium, 98.7 percent*

Each number adjoining an observation indicates the time, in hours, from the time of the initial observation

to 700° C in the third test, and contracted at various temperatures between 400° and 700° C. The expansion curves obtained in the fourth and fifth tests are smooth, except for a slight irregularity above 700° C. The observed contractions and irregularities probably were accompanied by evolution of hydrogen on heating the sample.

From the results on samples 1359A and 1328I, it is apparent that the linear thermal expansion of electrolytic chromium before it is stabilized by repeated heating may be affected by the temperature, hydrogen content or liberation, time and rate of heating, previous heat treatment, etc. After electrolytic chromium has been stabilized, the linear thermal expansion is a function only of the temperature.

Table 2 gives average coefficients of expansion which were computed for various temperature ranges from the expansion and contraction curves. The last column of the table shows the difference in length before and after each expansion test indicated.

From the coefficients of expansion obtained in the tests in which the expansion curves were smooth and free from irregularities (sample 1359A on tests 2 to 10, inclusive, and sample 13281 on tests 4 and 5), the following empirical equation was derived by the method of least squares:

$$a_t = (5.88 + 0.01548t - 0.00001163t^2)\ 10^{-6}, \qquad (1)$$

where a_t represents the instantaneous coefficient of expansion or the rate of expansion at any temperature, t, between $-75°$ and $+650°$ C. The probable error of a_t is $\pm 0.24 \times 10^{-6}$.

The curve representing the coefficients of expansion of the two samples of electrolytic chromium (99.3 and 98.7 percent) at various

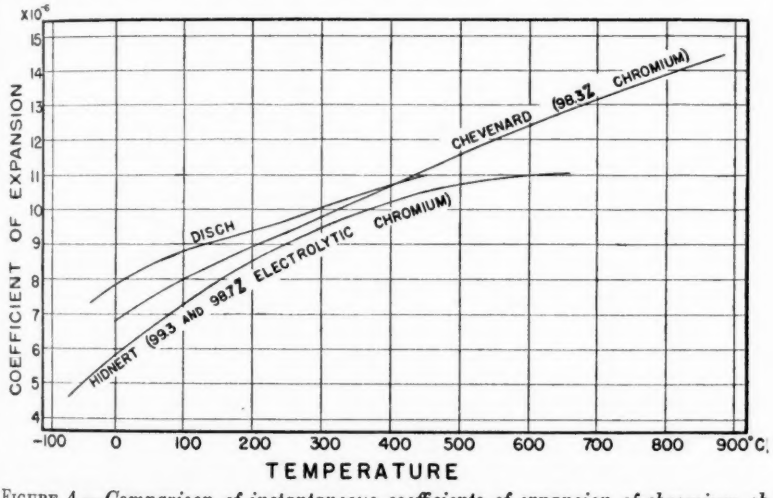

FIGURE 4.—*Comparison of instantaneous coefficients of expansion of chromium obtained in the present investigation and in previous investigations by Disch [4] and Chevenard [5].*

temperatures between $-75°$ and $+650°$ C, which was computed from eq 1, is shown in figure 4. This figure includes a curve derived from the data by Disch [4] on a sample of chromium of unknown purity and a curve from Chevenard [5] on a sample of chromium containing 98.3 percent of chromium.[3] Each of the curves is concave toward the temperature axis. At the lower temperatures, the

[3] Impurities principally aluminum and iron, but amounts were not indicated by Chevenard.

TABLE 2.—*Coefficients of linear expansion of electrolytic chromium*

Sample	Chromium content	Test method	Test[a]	Average coefficients of expansion per degree centigrade																		Change in length after heating and cooling[b]
				−100° to −50° C	−50° to −15° C	−15° to +20° C	+20° to 60° C	60° to 100° C	100° to 200° C	200° to 300° C	300° to 400° C	400° to 500° C	500° to 600° C	600° to 700° C	20° to 100° C	20° to 200° C	20° to 300° C	20° to 400° C	20° to 500° C	20° to 600° C	20° to 700° C	
	Percent			×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	*Percent*
			1H					[c]	[c]	[c]	[c]	[c]			[c]	[c]	[c]	[c]	[c]			−1.116
			1C						7.9						6.3	7.2			9.1			
		Precision comparator (air furnace).	2H				[d] 6.2	7.5	7.9	9.1	9.7	[c]			[d] 6.8	[d] 7.5	[d] 8.1	[d] 8.5	[c]			−0.020
			2C						7.8	9.3					6.9	7.4	8.1		9.0			
			3H				[d] 5.9	7.5	8.2	9.2	9.8	9.6			[d] 6.7	[d] 7.5	[d] 8.1	[d] 8.6	[d] 8.8			−.008
			3C						8.2	9.2					7.0	7.6	8.2		8.9			
			4H[a]	5.3	5.5	5.8	6.4	7.2							6.8							
1359A	99.3	Precision comparator (bath).	5H						8.1						6.6	7.5						
			6H						8.2						6.6	7.5						
			7H													7.5						
			8H[a]						8.1	9.2					6.7	7.5	8.1					+.002
			9H						8.2	9.0	9.2	10.1	[c]	[c]	6.8	7.6	8.1	8.4	8.7	[c]	[c]	−.048
		Precision comparator (air furnace).	9C				5.2	7.4	8.4	8.8	9.5				6.3	7.4	7.9	8.3				
			10H[a]						8.1	9.3	9.9	10.0	10.9	11.0	6.2	7.2	8.0	8.5	8.8	9.1	9.4	−.004
			1H				6.6	6.9	7.3	[c]					6.7	7.1	[c]					
			2H				6.6	6.9	7.3	[c]	[c]				6.8	7.0	[c]	[c]				
1328I	98.7	Interferometer (air furnace).	3H						7.8	9.2	[c]	[c]	[c]	[c]	6.7	7.3	8.0	[c]	[c]	[c]	[c]	
			4H						8.6	9.1	10.1	10.7	10.8	10.9	6.7	7.7	8.2	8.7	9.1	9.4	9.6	
			5H				5.7	7.1	8.2	9.0	10.0	10.6	11.0	11.9	6.4	7.4	8.0	8.5	8.9	9.3	9.7	(f)

[a] H indicates heating, and C, cooling.
[b] Determined from the expansion curve on heating and the contraction curve (or observation) on cooling. The plus sign indicates an increase in length and the minus sign a decrease in length.
[c] Evolution of hydrogen on heating.
[d] Published previously by author. (See reference 6.)
[e] Observations on cooling close to expansion curve on heating.
[f] After fifth test, sample was measured with micrometer and found to be 0.45 percent shorter than the initial length before first test.

coefficient of expansion increases rapidly with increasing temperature, but at higher temperatures the coefficient of expansion increases slowly. The coefficients of expansion obtained in the present investigation are less than those obtained by Disch [4] and Chevenard [5].

The following equation was obtained by integrating eq 1:

$$L_t = L_0 [1 + (5.88t + 0.00774t^2 - 0.00000388t^3)10^{-6}]. \quad (2)$$

In this equation, L_t represents the length at any temperature, t, between $-100°$ and $+700°$ C and L_0, the length at 0° C.

Table 3 gives a comparison of average coefficients of expansion of chromium computed from eq 2 and from data by Disch [4].

TABLE 3.—*Comparison of coefficients of expansion of chromium*

Temperature range	Average coefficients of expansion per degree centigrade	
	Present investigation[a]	Previous investigation[b]
°C	$\times 10^{-6}$	$\times 10^{-6}$
−100 to 0	5.1	[c]7.3
0 to 100	6.6	8.4
0 to 200	7.3	8.8
0 to 300	7.9	9.1
0 to 400	8.4	9.4
0 to 500	8.8	9.7
0 to 600	9.1	----------
0 to 700	9.4	----------

[a] Computed from eq 1.
[b] Computed by author from data by Disch [4].
[c] From −78° to 0° C.

V. DISCUSSION

Disch [4] stated that the sample of chromium which he investigated indicated a behavior similar to that of fused quartz. He found that this sample contracted on cooling until the temperature reached about −183° C, but it expanded on further cooling. He was unable to obtain accurate values, for the surfaces of the chromium sample deformed at low temperatures. The contraction between +20° and −183° C was 1.25 mm/m, and that between +20° and −190° C was 1.0 mm/m.

Chevenard [5] found that the linear thermal expansion of a sample of chromium (98.3 percent) was reversible between 0° and 100° C. His sample of chromium did not appear to have any thermal singularity between 0° and 900° C (See fig. 4).

The results by Hidnert [6] in 1931 and the present investigation indicate that irregularities in the linear thermal expansion of electrolytic chromium may be related to evolution of hydrogen. Grube and Knabe [9] also found irregularities in the temperature-resistance curves of electrolytic chromium, which they stated can be traced to the hydrogen content.

It appears to the author that the fine cracks which may be seen in some chromium plates subjected to temperature changes may be as-

cribed to evolution of hydrogen, which causes permanent shrinkage of the plates.

That the quantity of hydrogen liberated may be appreciable is also evident from the results reported by Adcock [10]. As a sample of carefully dried electrodeposited chromium lost 0.1 percent of its weight when heated to 900° C under vacuum conditions, he presumed that the metal contains about this percentage of hydrogen, which is in agreement with the value reported in 1931 [6] for chromium produced at the National Bureau of Standards. He stated that it seems definitely established that electrodeposited chromium also contains oxygen in some form.

From the results in table 1 it is evident that the density of the sample of electrolytic chromium (99.3 percent) increased 2.4 percent after 3 cycles of heating to 500° C and cooling to room temperature. The initial mass and volume of the sample were 37.954 g and 5.474 ml, respectively. After the three cycles of heating and cooling, the mass and volume were 37.978 g and 5.347 ml. In spite of evolution of hydrogen from the sample, its mass increased 0.024 g, or 0.06 percent. It appears that the sample oxidized during heating in air, and that more than 0.06 percent of oxygen, by weight, was absorbed by the sample. The volume of the sample decreased 0.127 ml, or 2.3 percent.

The first heatings of electrolytic chromium, which reduce or eliminate the content of hydrogen, affect other properties, as well as the linear thermal expansion. The electrical resistivity [5] of a sample of electrolytic chromium prepared at this Bureau decreased nearly 50 percent after heating to 500° C and cooling to room temperature. Additional heating to a higher temperature and cooling to room temperature caused a further decrease in the electrical resistivity. Adcock [10] found that the Brinell hardness number of electrolytic chromium decreased about 60 percent during heating to 900° C in vacuo. He found that the Brinell hardness number decreased still more if the chromium was treated with hydrogen at 1,500° to 1,600° C to remove oxide.

VI. SUMMARY AND CONCLUSIONS

The linear thermal expansion of two samples of electrolytic chromium (99.3 and 98.7 percent) was investigated at various temperatures between −105° and +715° C with a precision comparator method and with an interference method. A total of 15 tests was made.

The samples of electrolytic chromium contracted during the first heating when hydrogen presumably was evolved. It was possible to obtain smooth expansion curves after repeated heating.

After the first heating to 500° C and cooling to room temperature, the sample of electrolytic chromium containing 99.3 percent of chromium was 1.1 percent shorter than the initial length before heating. A smaller change was noted for the other sample of electrolytic chromium.

The linear thermal expansion of electrolytic chromium before it is stabilized, by repeated heating, is a function of the temperature, hydrogen content or liberation, time and rate of heating, previous treatment, etc. After repeated heatings of electrolytic chromium, the linear thermal expansion is a function only of the temperature.

[5] Information about electrical resistivity was furnished by I. L. Cooter, of this Bureau.

From the coefficients of expansion obtained in tests in which the expansion curves were smooth and apparently not affected by hydrogen, the following equations were derived:

$$a_t = (5.88 + 0.01548t - 0.00001163t^2)10^{-6} \quad (1)$$

and

$$L_t = L_0[1 + (5.88t + 0.00774t^2 0.00000388t^3)10^{-6}], \quad (2)$$

where a_t represents the instantaneous coefficient of expansion or rate of expansion at any temperature, t, between $-75°$ and $+650°$ C; L_0 represents the length at 0° C; and L_t the length at any temperature, t, between $-100°$ and $+700°$ C. Figure 4 and table 3 give coefficients of expansion computed from eq 1 and 2, and show comparisons with data from other observers.

The volume of the sample of electrolytic chromium containing 99.3 percent of chromium decreased 2.3 percent after three cycles of heating to 500° C and cooling to room temperature. The density increased 2.4 percent, for the mass of the sample increased only 0.06 percent.

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